

PROCEEDINGS
OF THE
NATIONAL ACADEMY OF SCIENCES
INDIA
1964

Vol. XXXIV

SECTION - A

Part III

POLARIMETRIC ESTIMATION OF BISMUTH

By

O. N. PERTI and I. PRAKASH

Chemical Laboratories, Th. D. S. B. Govt. College, Naini Tal

[Received on 6th January, 1964]

ABSTRACT

A rapid polarimetric estimation of bismuth ions in aqueous solutions is possible quite accurately. The method is based upon the fact that Bi⁺⁺⁺ions in aqueous solution form a soluble complex of potassium bismuth tetra-iodide in presence of excess of potassium iodide. The complex of iodide of bismuth and potassium is precipitated completely by addition of aqueous solution of quinine sulphate resulting in formation of optically active complex. This active complex is properly washed, dissolved in mixture of acetone and hydrochloric acid solution and estimated polarimetrically at the room temperature. The following equation, which has been derived on the basis of experimental data, expresses the linear relationship between concentration of bismuth ions ($Y = \text{mgs Bi}/100 \text{ ml.}$) and optical rotation of complex in degrees (x)

$$Y = 1.684 + 106.8x = \text{mgs Bi}/100 \text{ ml.}$$

INTRODUCTION

It is well known that aqueous solutions of several optically active alkaloids or their salts precipitate almost quantitatively the cations from solution, yielding

optically active complex. Recently C. Liteanu and M. Cosma¹ have made use of such complexes in carrying out the estimation of mercury by measuring the optical rotation of complex formed by quinine with potassium-iodo-mercurate. They measured optical rotation of different concentration of solutions, containing Hg⁺⁺ ions by first converting it into tetra-iodo-mercurate with the help of potassium iodide and then precipitating with quinine-mono-chloro hydrate solution. The properly washed precipitate was dissolved in acetone and solution thus obtained was subjected to polarimetric measurement at the room temperature. A plot of rotation against concentration showed a straight line from which a relationship

$$Y = -7.1 + 1.433x = \text{mgs Hg}/100 \text{ ml.},$$

where x = angle of rotation expressed in $l/100^\circ$, could be deduced. In a previous communication the authors have described polarimetric estimation of cadmium.² In the present paper authors have given a similar method for polarimetric determination of Bi⁺⁺⁺ ions in solution.

EXPERIMENTAL

Korenman³ recommended brucine and potassium iodide for detection of Bi⁺⁺⁺ ions in very dilute solutions. He detected presence of bismuth ions by adding a few drops of saturated solution of potassium iodide and solution of brucine to 1 ml. of solution of salt to be tested. A yellow precipitate, insoluble in dilute hydrochloric acid was obtained. The sensitivity of this reaction was 1:720,000. A colour was visible at a dilution of 1:600,000 if brucine solution was substituted by aqueous solution of quinine sulphate.⁴ Due to higher optical rotary power of aqueous solution of quinine sulphate as compared to solution of brucine, authors decided to use quinine sulphate in conjunction with potassium iodide for quantitative precipitation of bismuth ions in the form of an optically active complex.

The estimations were carried out by using different amounts of bismuth nitrate solutions containing 5 gms in 500 ml. The volumes of solution taken for different estimations were from 3 ml. to 30 ml., corresponding to 12.78 mgs to 127.8 mgs of bismuth ions. To each of these solutions was added potassium iodide solution (40 gms/litre) equal to volume of solution of bismuth nitrate taken. To this solution was added an excess of 1.5% solution of quinine sulphate. A orange

precipitate of an optically active complex was obtained which was filtered and washed a couple of times with cold water and finally with petroleum ether. The precipitate was then dissolved in 60 ml. of acetone and volume was raised to 100 ml. by adding 40 ml. of dilute hydrochloric acid solution. It was noticed that the addition of the acid clears up the solution. Polarimetric measurements were carried out with this solution, using a two decimeter tube at room temperature (10 – 12°C.).

To check the amount of bismuth ions in solution a separate sample of original solution was gravimetrically estimated using 8-hydroxy-quinoline.⁵

In table I values of optical rotation are mentioned corresponding to different amounts of bismuth ions, present in solution of bismuth nitrate taken for polarimetric measurements. The least count of the instrument used was 0·01°.

TABLE I

Optical rotation of solutions containing different amounts of Bi⁺⁺⁺ions
in the form of optically active complex

Serial Number	mg. Bi ⁺⁺⁺ /100 ml.	Optical rotation in degrees for Hg 5461
1	12·78	0·10
2	25·57	0·23
3	38·35	0·35
4	51·13	0·44
5	63·92	0·62
6	85·22	0·76
7	106·5	0·97
8	127·8	1·19

DISCUSSION

A plot of concentration against observed optical rotation shows a linear relationship (fig. 1).

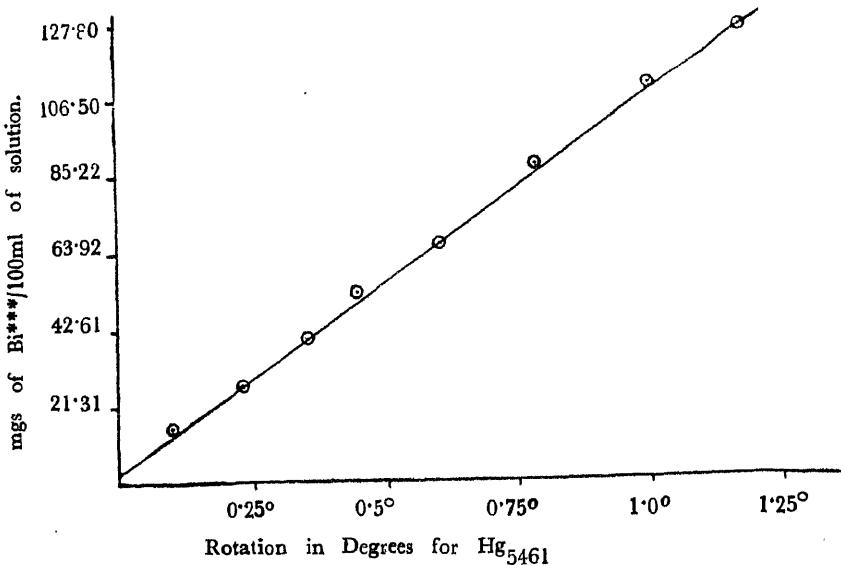


Fig. 1. Relation showing between mgs $Bi^{++}/100ml$ and optical rotation in degrees.

The equation of the curve was calculated by the method of least squares and the following expression was obtained.

$$Y = 1.684 + 106.8x = \text{mgs. Bismuth}/100 \text{ ml.}$$

where x is the angle of rotation in degrees and Y is concentration of bismuth ions in mgs per 100 ml. This is an empirical equation based on experimental observations. The constant in this equation indicates that the experimentally obtainable curve does not pass exactly through the origin (fig. 1) as it ought to do theoretically. However, the experimental curve calculated from experimental data by the method of least squares is found to have better utility so far as the estimation of the metal ion is concerned. It may be mentioned that similar results were obtained by Liteanu and Cosma.¹ These are empirically derived curves from experimental data with limited accuracy and hence the best fit with the data is not exactly that which would be obtained theoretically.

In table 2 a comparison is made between gravimetrically estimated values of bismuth ions and the values obtained from empirical equation referred above, for different volumes of solution.

TABLE 2

A comparison of amount of Bi⁺⁺⁺ present in different volumes of solution by gravimetric estimation and polarimetric estimation

S. N.	Volume of Bi (NO ₃) ₃ solution taken in ml.	Amount of Bi ⁺⁺⁺ ions in mg. Gravimetric Estimation (a)	Amount of Bi ⁺⁺⁺ ions in mg. Polarimetric Estimation (b)	Difference in mgs. (a) — (b)
1	3	12.78	12.36	+ 0.42
2	6	25.57	26.25	- 0.68
3	9	38.35	39.06	- 0.71
4	12	51.13	48.68	+ 2.45
5	15	63.92	67.90	- 3.98
6	20	85.22	82.85	+ 2.37
7	25	106.5	105.3	+ 1.2
8	30	127.8	128.8	- 1.0

It is quite evident from table 2 that polarimetric estimation of bismuth ions gives fairly accurate results even in fairly dilute solution of bismuth salt. It is also clear that accuracy of polarimetric estimation increases in higher concentration of bismuth ions. Polarimetric estimation of concentrated solutions, having more than 0.13 gm of Bi⁺⁺⁺ ions per 100 ml is not possible due to deepening of colour of solution, through which light does not pass easily. However polarimetric measurement is possible by diluting the concentrated solution. Similarly the method is apparently not very suitable for direct estimation of solutions containing less than 0.013 gm of bismuth ions per 100 ml. In all such cases, however, the solution can be concentrated and the polarimetric estimations can be carried out with fair degree of accuracy.

CONCLUSION

Estimation of bismuth ions in aqueous solutions can be carried out quite rapidly with a fair degree of accuracy polarimetrically. For this purpose bismuth ion is first converted into potassium bismuth-tetra-iodide by addition of potassium iodide. Bismuth ion, from potassium bismuth-tetra iodide, is precipitated with the help of aqueous solutions of quinine sulphate to yield an optically active complex which is isolated, dissolved in a mixture of acetone and hydrochloric

acid solution and measurement of optical rotation of the complex is done quite rapidly. Thus estimation of Bi⁺⁺⁺ions can be carried out with the help of the empirical equation, deduced on the basis experimental data. The most suitable concentrations of Bi⁺⁺⁺ions for polarimetric estimation are 0·013 gm to 0·13 gm per 100 ml. of solution.

ACKNOWLEDGEMENT

The authors feel obliged to authorities of Th. D. S. B. Government College, Naini Tal for provision of research facilities. They also offer their thanks to Dr. B. R. Singh for this valuable suggestions and help in experimental work.

REFERENCES

1. Liteanu, C. and Cosma, M., *Talanta* 1961 8 (5), 313-316; *Analytical Abstracts*, 9, no. 48 Jan. 1962.
2. Perti, O. N. and Prakash, I., *Proc. Nat. Acad. Sci. (India)*, A, 34, 1 (1964).
3. Korenman, I. M., *Z. anal. Chem.*, 99, 402-10 (1934); *C. A.* 29, 1358 (1935).
4. Aubry, P., *Analyst*. 47, 129 (1922).
5. Vogel, I., *Quantitative Inorganic Analysis* (Second Editson) (Longmans,) Page 427.

HYOSCINE IS THE CHIEF CONSTITUENT OF DATURA
SUAVEOLENS LEAVES

By

B. K. GUPTA, VISHWA PAUL, K. L. HANDA and L. D. KAPOOR

Regional Research Laboratory, Jammu

[Received on 11th July, 1963]

ABSTRACT

Datura suaveolens leaves growing in Northern India contains alkaloids mainly consisting of Hyoscine.

Datura suaveolens Humb & Boupl ex Willd. (*Brogmansia suaveolens* G. Don) is a handsome shrubby plant with large fragrant flowers. It is native of Mexico and is often raised in the gardens of upper Gangetic Plains of India. Investigation of the leaves was initiated, because study of available literature did not indicate any previous assessment of its potentialities.

The leaves for investigation were obtained from Dehradun side. These were found by Indian Pharmacopoeia assay method to contain 0·21% of the total alkaloids, calculated as hyoscyamine. 160 g of the air dried powdered drug, when processed as usual, yielded about 0·57 g of the crude bases. These were split up into 9 fractions by King and Ware's method¹. The first eight fractions which formed 65% of the total, when chromatographed on Whatman No. 1 paper using solvent systems S₁-BuOH : HCOOH : H₂O : 4: 1: 5 and S₂-BuOH : Et OH : 2N HCl :: 4 : 1 : 2 and sprayer Modified Dragendorff's reagent,² revealed only one spot of Rf values in S₁ 0·42 and in S₂ 0·61 corresponding to that of hyoscine. To settle the identity of these eight fraction with hyoscine, only eighth fraction was converted to gold chloride derivative. The mixed m. p. with an authentic hyoscine aurichloride remained undepressed. The 9th fraction, having two spots on the chromatogram, was refractionated into four fractions by the above method. Of these four, first three, equal to 40% of it, were found by chromatography to be hyoscine and the fourth a mixture of hyoscine and hyosyamine (Rf. values in S₁ 0·42 and 0·55 in S₂ 0·61 and 0·70 respectively).

Method for preparation of Hyoscine hydrobromide from Datura suaveolens leaves.—The powdered dry leaves were extracted by cold percolation with alcohol till exhaustion.¹ The alcoholic extract was concentrated in *vacuo*. From this the total alkaloids were taken in 1N H₂SO₄; wherefrom after basification with sodium bicarbonate to pH 8, only hyoscine was got extracted with chloroform. The

yield of the hyoscine by this method was more than 90% of the theoretical. This was neutralised with alcoholic hydrobromic acid and hyoscine hydrobromide thus obtained was charcoalised and then crystallised from alcohol.

It appears, therefore, that the alkaloids of *Datura suaveolens* leaves consist mainly of hyoscine (about 80%) and can be exploited for the preparation of hyoscine hydrobromide which is being imported at present.

REFERENCES

1. King, Harold, and Ware, Lancelot L., *J. Chem. Soc.*, 1941, 331.
2. Munier, R., and Mecheboeuf, H., *Bulletin de la Societe de Chimie biologique*, 32, 192, 304 (1950).

MASS MEASUREMENTS IN NUCLEAR EMULSIONS

By

A. P. SHARMA

Department of Physics, Aligarh Muslim University, Aligarh

[Received on 14th October, 1963]

ABSTRACT

A method for the determination of mass of charged particles in nuclear emulsions is described. On the basis of selection criteria the use of two most sensitive ionization parameters i.e. the integral gap-length and the probability of development parameters has been made and the results are found to be very satisfactory. The verification of the results has been done by additional methods.

1. Introduction :

For mass measurements of the particles of small charge, the counting of the number of grains (grain density) along the trajectory recorded by a charged particle is as old a method as the emulsion technique itself. But in this case the proportionality between grain density and specific energy loss which exists for low ionization ceases to be valid for the ionization greater than four times its minimum value caused by a particle of unit charge and relativistic speed. With greater ionization, the grains overlap each other and hence their counting becomes purely subjective and sometimes impossible (Fowler)¹. To overcome these difficulties Hodgson², Renardier *et al*^{3,4} and Kayas⁵ have recommended the counting of gaps or blobs along the trajectory as these measurements are more objective than the grain counting.

In gap or blob counting which are equivalent terms, a number of difficulties e.g. (i) the resolution of grains depending on the quality of the optical image and the observer, (ii) the mean size of the developed grain, (iii) the correction for dip of the track and (iv) the slow variation of the gap density with specific ionization in a certain important range of values, are encountered and hence the measurement of the length of gaps is considered more useful (Hodgson², Renardier³) O'Ceallaigh^{6,7} measured an exponential distribution of the length of gaps in tracks of particles with widely different specific ionization. According to Fowler and Perkins⁸, the reciprocal of mean gap length is shown to be insensitive to the mean grain size and hence provides a satisfactory measure of the ionization and mass of heavy mesons.

All such measurements depend on the development factor of the emulsion and hence the normalization with respect to minimum ionization tracks is always necessary. In our communications (Sharma⁹; Sharma and Gill^{10,11,12}) we have

emphasized the importance of the parameter π , the probability of development of a grain which is independent of development of the emulsions and hence has safely been utilized by us (Sharma⁹, Sharma and Gill¹²) for determining the charge of heavy primaries of cosmic radiation.

In this paper an attempt has been made to use this probability of development parameter as well as the integral gap length for the determination of mass of heavy mesons. The experimental results obtained are quite in agreement with the results of other workers. The verification of the results has also been done by some additional crossover methods.

2. Experimental Details:

Two stacks* consisting of 200 and 125 sheets of 6 in. \times 6 in. \times 600 μ Ilford G-5 emulsion strips and exposed to cosmic radiation in Baloon flights for about 8 hours and 3 hours above 60,000 feet at geomagnetic latitudes of 19°N and 15°N (India) respectively during Feb.-March, 1954, were selected for the experiment. An analysis was made of 5 τ -mesons disintegrating at rest into three singly charged secondary *i.e.* L-meson, 2 K-mesons giving a star, and 4 Σ -hyperons. All primary meson particles were stopping in the emulsion. The measurements were done only on the primary mesons before disintegrating into their secondaries.

The measurements were done on the Bausch & Lomb microscope having an oil immersion objective of 97 \times (N.A. = 1.25) and a filar micrometer (Goniometer attached with Ernst Leitz Ocular) eyepiece of 10 \times carrying a fine scale attached with a small drum of rotating head with 100 divisions on its circular scale. Each division of the drum recorded 0.0415 μ . The arrangement of aligning the track and its motion along an axis (x or y) was extremely fine. The latter arrangement was done by connecting a large drum carrying 500 divisions on it and whose each division was equal to one micron. The arrangement allowed an easy and accurate alignment of the gap edges with the hair of the drum micrometer.

3. Selection of an Ionization Parameter:

As the plateau grain densities in the stack A and stack B were 28.25 grains/100 μ and 22.5 grains/100 μ respectively, the reasonable grain counting could only be possible in these stacks upto 3 times and 4 times the minimum ionization respectively and hence the gap and blob countings were considered preferable and less subjective even in the regions of high energy losses.

For making a selection of a suitable ionization (gap or blob) parameter sensitive to specific energy losses along the particle trajectory, the measurements were made for various gap parameters for different particle tracks (π -meson, K-meson and proton tracks) available in the stacks mentioned earlier. The results are shown

* The use of stacks was made due to the courtesy of Prof. M. G. K. Menon and Dr. R. R. Daniel, T.I.F.R., Bombay.

in fig. 1 and 2 and also in Table 1. In this table, the parameters N , L_g , I_g , \bar{L}_b , \bar{l}_b denote the total number of blobs, total gap length, mean gap length, total blob length and mean blob length respectively.

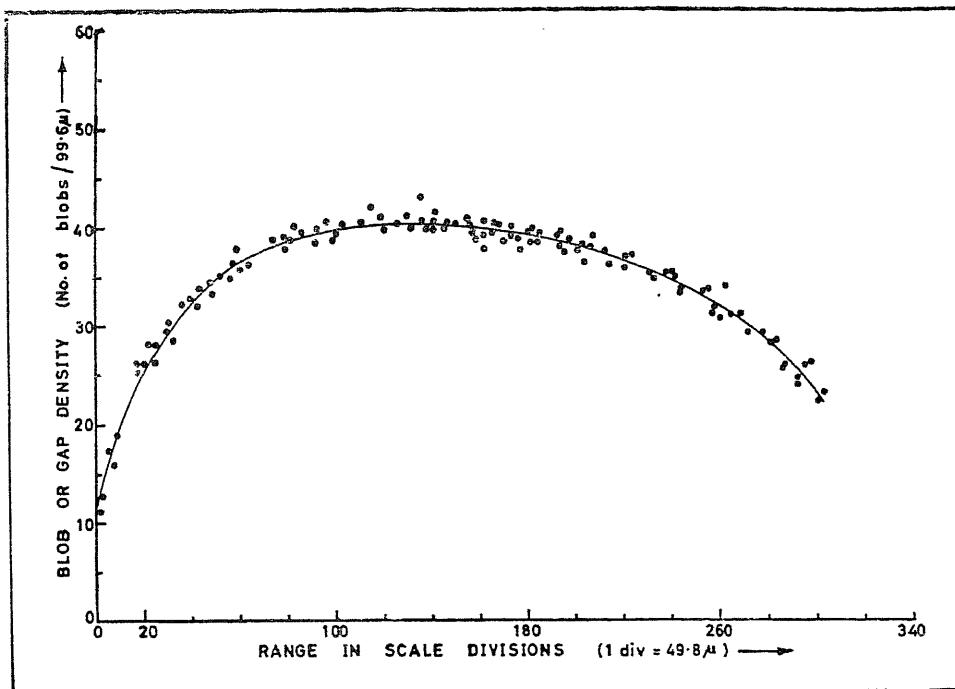


Fig. 1. Variation of Blob or Gap Density (n_b or n_g Per 99.6μ) with Residual Range for Tracks of π Mesons in Stack A.

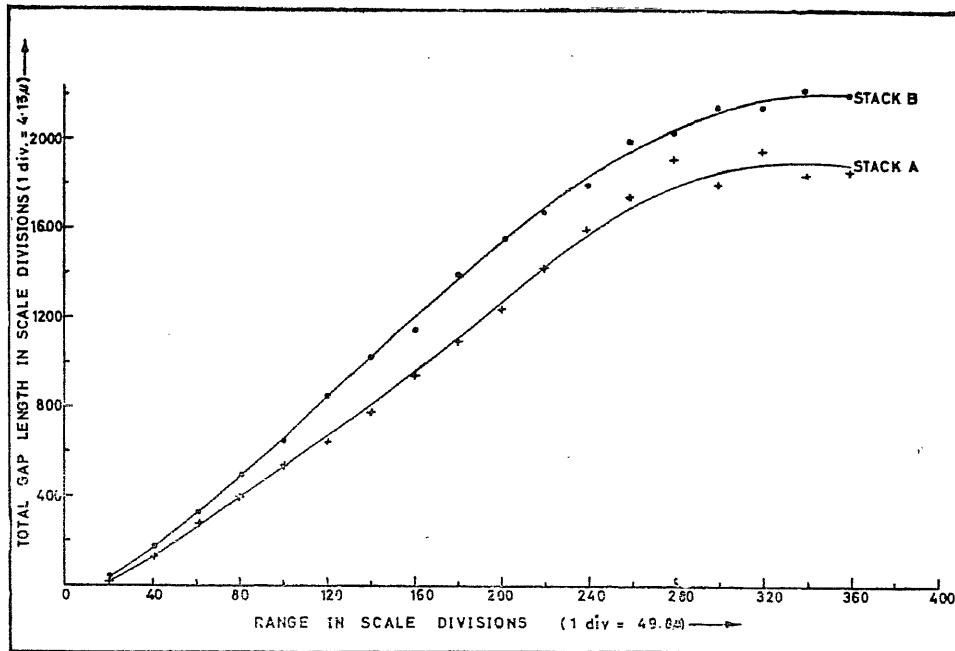


Fig. 2. Variation of Total Gap Length (L_g) with Residual Range for Tracks of K-Mesons in Stack A and Stack B.

TABLE I
Ionization parameters for various particles at the end of their range

Particle track	Parameter used	Segments of tracks at the end of track in scale dvns. ($dv = 0.0415 \mu$)				Ratio of columns (d) and (a)	
		(a) 0-2400	(b) 2400-4800	(c) 4800-7200	(d) 7200-9600		
π -mesons	...	N	22	24	27	30	1.36
		L_g	431.5	540.2	630.5	691.4	1.60
		l_g	19.61	22.50	23.35	23.05	1.17
		L_b	1968.5	1859.8	1769.5	1708.6	0.87
		l_b	89.47	77.49	65.54	56.95	0.64
K-mesons	...	N	17	18	21	23	1.35
		L_g	255.6	380.2	410.1	457.5	1.79
		l_g	15.04	21.12	19.53	19.89	1.32
		L_b	2144.4	2019.8	1989.9	1942.5	0.91
		l_b	126.1	112.21	94.76	84.46	0.70
Protons	...	N	15	16	18	20	1.33
		L_g	230.6	250.1	325.3	400.2	1.74
		l_g	15.37	15.63	18.07	20.01	1.30
		L_b	2169.4	2149.9	2074.7	1999.8	0.92
		l_b	144.63	134.37	115.26	99.9	0.69

According to Fig. 1 the variation of blob or gap density indicating an increase with the residual range passes through a maximum and then diminishes with decrease in specific ionization. This is due to the fact that the average dimension of the blobs becomes smaller as we go farther from the end of the track and then diminution occurs when the ionization is such that the number of blobs is small in comparison to the number of isolated grains. The variation of gap density is identical with that of the blobs.

According to table 1, the parameter l_g increases by 17% in the case of π -meson and 30% in case of K-meson and protons. Similarly, the parameter N increases by nearly 33-36%, but the total gap length L_g increases by 60-88%. The total blob length at the end is nearly constant throughout and l_b diminishes by nearly 30%. Hence the parameter L_g is most sensitive to specific energy loss variations and their measurements at the end of the range of stopping particles, while in the regions of small ionization the parameter L_b is reasonably sensitive one. Similar results for some of these parameters have also

been indicated by Tsai Chu and Claret¹⁸ for proton tracks alone. Thus on the basis of these observations, a selection of the parameter L_g (total gap length of all gaps) has been made for determining the mass of the particles at the end of the tracks where the ionization is very high.

In table 2 are shown the results of the probability of development of a grain (π) for various energy losses and it has been shown that the variation in π at the small ionization regions is much sensitive and at high ionization it is constant as indicated by the ratios $\sim (65)$ and $\sim (95)$ respectively nearing low and high ionization regions.

TABLE 2
Probability of development π and its Sensitiveness to specific energy loss variations

dE/dR interval in Mev/gm cm ⁻²	Experimental values of π	Ratios of alternate values of π (e.g. 0.085:0.147 0.133:0.190 etc.)
2-3	0.085	
3-4	0.133	0.64
4-5	0.147	
5-6	0.190	0.66
6-7	0.221	
7-8	0.250	0.83
8-9	0.268	
9-10	0.301	0.88
10-11	0.305	
11-12	0.318	0.90
12-13	0.340	
13-14	0.359	0.88
14-15	0.388	
15-17	0.399	0.92
17-19	0.420	
19-21	0.425	0.96
21-23	0.439	
23-25	0.459	0.94
25-27	0.468	

Hence, the parameter π was more efficiently utilized at low ionization regions of the long tracks of heavy means in the present experiments and the total gap length L_g parameter was used at the end of these tracks.

4. Relation between the Ionization Parameters and the Mass of Charged Particles.

Renardier *et al*⁴ and Kayas⁵ have shown that the total number of gaps (voids), N_g , as a function of the residual range is of the form,

$$N_g = \bar{K}' \cdot R^{\alpha'} \quad \dots \dots \dots \quad (1)$$

Where K' and n' are the constants characteristic of the degree of development of the emulsion and capable of being determined experimentally by means of the particles of known mass. Infact, K' depends on the mass of the particle which enters implicitely as a parameter in the above relation and n' represents the slope of the curve.

Assuming the validity of the relation (1) for total number of all gaps vs range, the relation for total length of all gaps vs range can also be assumed of the form,

$$L_g = K' R^{n'_1} \dots \dots \dots \quad (2)$$

The values of the exponents n' and n'_1 in the above two relations obtained by different authors are shown in table 3: For finding these exponents, we have measured the lengths of all gaps and their number for long tracks of 10 π -mesons from $\pi-\mu$ decay events, 6 protons whose identity was made certain by scattering measurements with the scheme of Fay *et al*¹⁴ and 6 K-mesons found in two G-5 emulsion stacks (stack A and stack B). Only those tracks were selected for measurement which had a very small slope of $\leq 10^\circ$ with respect to the plane of the emulsion. The least count of the eye-piece scale of the microscope was 0.0415μ . The results are shown in figures 3 and 4.

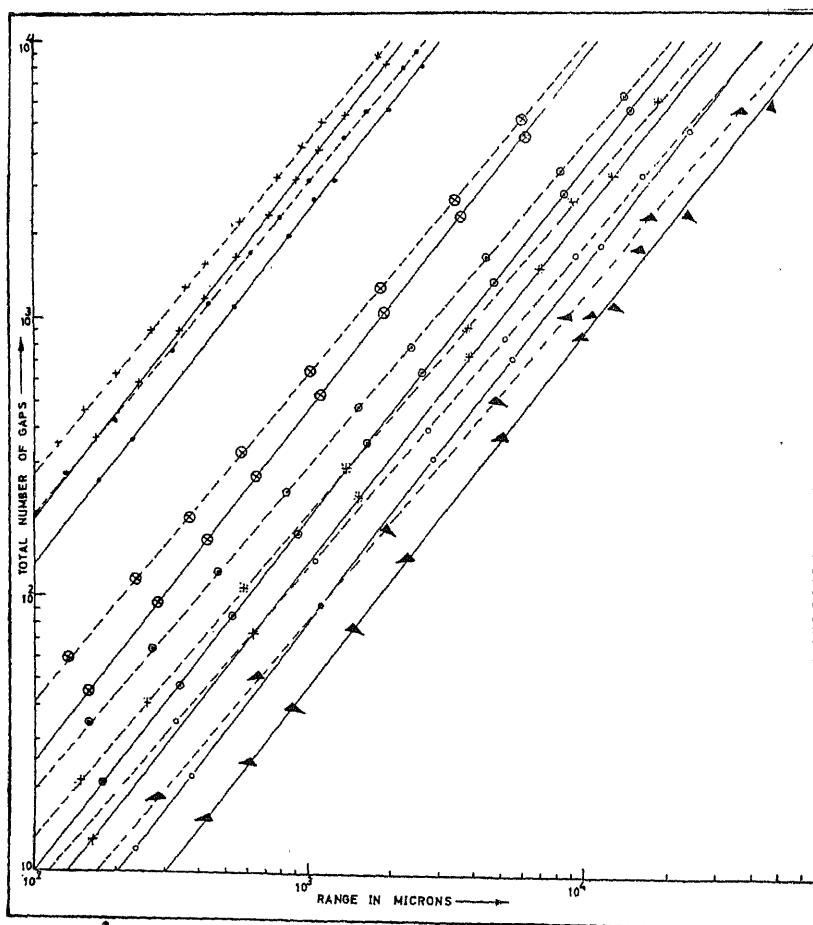


Fig. 3. Variation of Total Number of Gaps or Blobs with Residual Range for Particles μ -Meson (X), π -Meson (●), K-Meson (◎), Proton (○), Σ -Hyperon (✖), Deuteron (○) and Triton (▲) on Double Log Scale. The Continuous Curves are for Stack A and the Broken Curves are for Stack B.

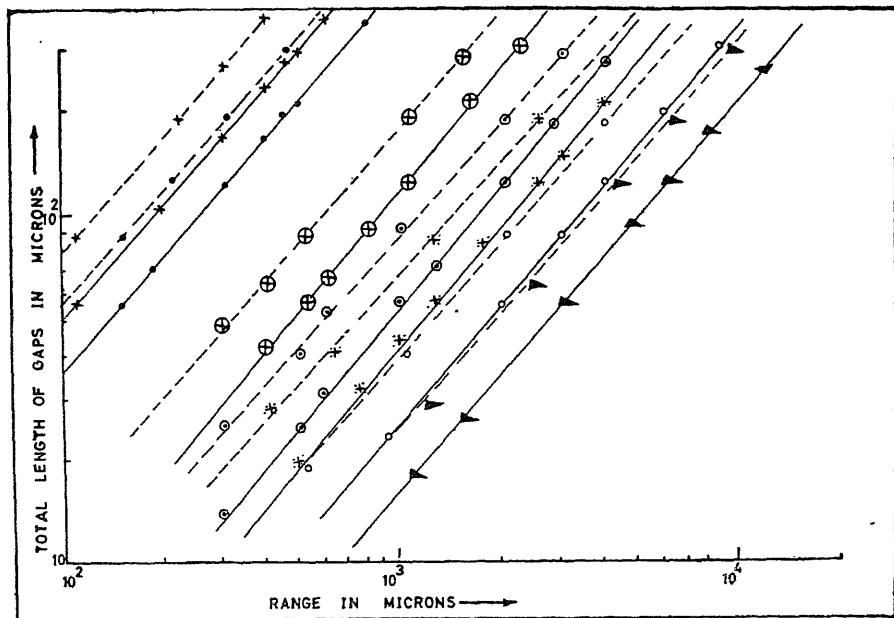


Fig. 4. Variation of Total Gap Length with Residual Range for Particles μ -Meson (X), π -Meson (\bullet), K -Meson (\oplus), Proton (\circ), Σ -Hyperon ($*$), Deuteron (\circ) and Triton (\blacktriangle) on Double Log Scale. The Continuous Curves are for Stack A and Broken Curves are for Stack B.

TABLE 3
Values of the constants n' , n'_1 , K' , K'_1 .

Workers	Constants			
	n'	n'_1	K'	K'_1
Hodgson ²	1.45	—	—	—
Kayas ⁵	—	1.32	—	—
Baroni and Castagnoli ¹⁵	1.43	1.29	—	—
Present work	Stack A. 1.288	1.162	0.027	0.018
	Stack B. 1.187	1.071	0.080	0.054

As the relation $\frac{L}{M} = F \frac{R}{M}$ is valid for all particles of the same charge

and may be approximately represented by the following straight line relation,
 $\log(L/M) = \log K'_1 + n'_1 \log(R/M)$ (3)

Hence for two particles having the same L (Tsai-Chu and Claret¹³).

$$\frac{M_1}{M_0} = \frac{R_1}{R_0}^{n'_1/(n'_1 - 1)} \quad \dots \dots \quad (4)$$

Substituting the experimental value of n' in the above relation (4) and assuming the mass (M_0) of the comparison or reference particle (proton) as unity, the unknown mass M_1 can be calculated from the following relation.

$$M_1 = \frac{R_1}{R_0}^{7.173} \quad \text{for stack A},$$

$$\text{and } M_1 = \frac{R_1}{R_0}^{15.08} \quad \text{for stack B},$$

} (5a)

Where R_1 is the residual range of unknown particle and R_0 that of the known one.

Similarly for particles having the same R ,

$$M_1 = (L_0/L_1)^{1/n' - 1}$$

$$\text{or } M_1 = (L_0/L_1)^{6.173} \quad \text{for stack A}$$

$$\text{and } M_1 = (L_0/L_1)^{14.06} \quad \text{for stack B}$$

} (5b)

where L_1 is the total gap length of unknown particle and L_0 that of the known one.

The above equations (5) allow the determination of the mass at the end of the range.

5. Other methods used for the determination of mass of heavy mesons.

Apart from the method described as above (section 4) for the measurement of masses of heavy mesons or other particles which stop in the emulsion, we had at our disposal two other methods so that a proper checking of the experimental results may be done. These controlling methods or cross-checkings for each particle allow the evaluation of the accidental errors due to either the imperfection of the emulsion or of the measuring apparatus and offer the advantage of increasing the precision of the mass estimated of each particle. One of the methods mentioned below associates ionization with range while the second one associates coulomb's multiple scattering with range.

(i) Gap density vs range.

and (ii) Scattering vs range.

(i) *Gap density vs. range Method.*

Since the total number of gaps (N_g) in a track is a function of the initial particle energy, hence for particles of unit charge,

$$N_g = K' M^{1-n'} R^{n'} \quad \dots \quad (6)$$

Where M is the mass of the unknown particle in proton mass units, and K' the ordinate at the origin of the straight line corresponding to the reference particles (protons) whose mass is taken as unity.

Taking log on both sides of equation (6), an expression for the mass of the unknown particle can be written as,

$$\log M = \frac{1}{n' - 1} (\log K' - \log N_g + n' \log R) \quad \dots \dots \dots \quad (7)$$

Substituting the values of n' and k' from Table 3 in the above relation, we will have for stack A and B the following relations respectively.

$$\log M = -5.447 + (4.472 \log R - 3.472 \log N_g)$$

$$\text{and } \log M = -5.866 + (6.348 \log R - 5.348 \log N_g) \quad \dots \dots \dots \quad (8)$$

Hence knowing N_g values at various residual ranges, the unknown mass can be calculated from equation (8).

(ii) Scattering vs range method.

The measurements of scattering were made with the sagitta method for finding the mass of heavy mesons stopping in the emulsion. The constant sagitta scheme of Fay *et al*¹⁴ has been applied, but we have made its calibration for the mean deviation \bar{D} .

The calibration of the constant sagitta method has been done with the tracks of 5 π -mesons from $\pi - \mu$ decay events, 3 protons and 2 τ -mesons with three observable charged secondaries. By applying all usual corrections, we have found the mean deviation \bar{D} equal to $0.502 \pm 0.014 \mu$ while the value of \bar{D} according to the scheme of Fay *et al*¹⁴ was 0.5μ for protons, τ -mesons and π -mesons of masses M_p , M_τ or M_π respectively as shown in relation (9). According to the relation of Fay *et al*¹⁴ and with our corrected mean deviation value, the mass M_x of an unknown particle (heavy mesons) may be calculated from the following relation applicable to singly charged particles,

$$\frac{0.502 \pm 0.014}{\bar{D}_x} = \left\{ \frac{M_x}{M_{p, \tau, \pi}} \right\}^{0.43}$$

or

$$\left\{ \frac{M_x}{M_{p, \tau, \pi}} \right\} = (0.502 \pm 0.014/\bar{D}_x)^{2.326} \quad (9)$$

Where $M_{p, \tau, \pi}$ represents the masses of the proton ($1837 m_e$), τ -meson ($966 m_e$), and π -meson ($273 m_e$) and \bar{D}_x represents the mean deviation obtained for unknown particle using the constant sagitta scheme for proton, τ -meson or π -meson with $\bar{D} = 0.5 \mu$.

6. Results of mass measurements of heavy mesons:

The three methods of mass measurements *i.e.* gap length, gap density and multiple scattering mentioned in the previous sections (4) and (5) have been applied for the determination of mass of heavy mesons. The results for 5 τ mesons decaying into three charged particles, 5 K -mesons giving a single charged particle, 2 K^- -mesons giving a capture star and 4 Σ -mesons (hyperons) nearly all of them decaying at rest are shown in Table 4.

TABLE 4
Results of mass measurements on heavy meson tracks

Particle	Origin (source)	Range (mm.)	Stack No.	Energy (MeV.)	No. of emulsions traversed	Nature of charge	Mass values from 3 methods in m_e				
							Mode of decay	Gap length (I)	Gap density (II)	Multiple scattering (III)	Weighted average (I) + (II) + (III)
π_1	$9 + \frac{1}{2}n$	B	87.00	140.0	90	+	$\rightarrow 2\pi^+ + \pi^- + \gamma$ ray	976 ± 42	982 ± 20	992 ± 38	982 ± 20
π_2	26 + 2 p	A	41.00	90.0	27	+	$\rightarrow 2\pi^+ + \pi^-$	970 ± 30	950 ± 10	981 ± 35	967 ± 16
π_3	22 + 5 p	A	22.00	62.0	31	+	$\rightarrow 2\pi^+ + \pi^-$	950 ± 60	990 ± 20	973 ± 51	971 ± 27
π_4	8 + 1 p	A	11.50	42.5	8	+	$\rightarrow 2\pi^- + \pi^+$	964 ± 30	947 ± 42	992 ± 48	968 ± 23
π_5	12 + 6 p	B	9.70	39.0	7	-	$\rightarrow 2\pi^- + \pi^+$	962 ± 50	930 ± 120	1011 ± 90	968 ± 52
K_1	21 + 2 p	B	19.22	58.0	7	+		930 ± 60	982 ± 42	1070 ± 20	994 ± 70
K_2	13 + 0 n	B	8.27	35.5	1	+		960 ± 101	990 ± 40	980 ± 110	977 ± 49
K_3	13 + 2 p	A	14.75	49.0	2	+	\rightarrow Single fast charged pion.	954 ± 90	910 ± 52	1030 ± 32	965 ± 36
K_4	-	A	76.73	130.0	16	+		955 ± 60	920 ± 56	998 ± 50	958 ± 32
K_5	16 + 0 n	B	5.10	27.0	2	+		990 ± 80	919 ± 110	1021 ± 170	977 ± 73
K_6	-	B	16.45	52.0	17	+		980 ± 112	990 ± 150	940 ± 20	970 ± 41
K_7	7 + 8 p	A	2.90	19.5	1	-	Capture in Star.	965 ± 80	970 ± 110	1038 ± 150	991 ± 67
K_8	-	B	29.10	74.0	5	-		980 ± 90	1008 ± 95	1065 ± 70	1018 ± 60
Mean of π, K^+ and K^- modes											
Σ_1	-	A	29.09	74.0	5	+		2435 ± 150	2460 ± 200	2470 ± 160	2455 ± 99
Σ_2	-	B	3.23	21.0	4	+	$\rightarrow p$	2390 ± 120	2260 ± 250	2398 ± 250	2349 ± 124
Σ_3	-	B	2.73	19.0	1	+		2501 ± 350	2225 ± 300	2430 ± 300	2385 ± 183
Σ_4	-	A	8.33	35.75	2	+		2210 ± 200	2321 ± 190	2425 ± 140	2319 ± 103
Mean of Σ particles											
	-	-	-	-	-	-		2384 ± 112	2317 ± 119	2431 ± 112	2377 ± 60
								966 ± 23	967 ± 27	1016 ± 33	983 ± 16

7. Discussion of results and conclusion:

In table 1 and 2 are shown the results of measurements of ionization parameters for various particles at the end of their range where the ionization is very high and also far away from it where the ionization is less. For observing the sensitivity of the parameters at the end of the range nearly 400μ residual range has been divided into four equal segments and the corresponding ratios of gap parameters are found. The results conclude that the gap length parameter is most sensitive for measurements at the end of the range while the probability of development (π) parameter is quite sensitive in less ionizing regions. Table 3 gives the values of the constants for total gaps and total length vs range relations for two stacks and the relation (5) has been derived for determining the mass of the heavy particles (K -mesons and hyperons). Equation (8) gives a method of determining the mass of charged particles by blob density measurements. A calibration has been done for the mean deviation D of constant sagitta scheme of multiple scattering given by Fay *et al*¹⁴. The magnitude of the deviation D is found as $0.502 \pm 0.014\mu$ while the value of D according to scheme of Fay *et al*¹⁴ is as 0.50μ . Relation (9) gives a measure of the unknown mass M_x of a particle in comparison to the mass of proton, τ -meson or π -meson for the specific scheme used.

A test of uniformity was made by measuring blob and grain densities for every sheet of the emulsion and it was found (Fig. 5) that the emulsions were developed quite uniformly.

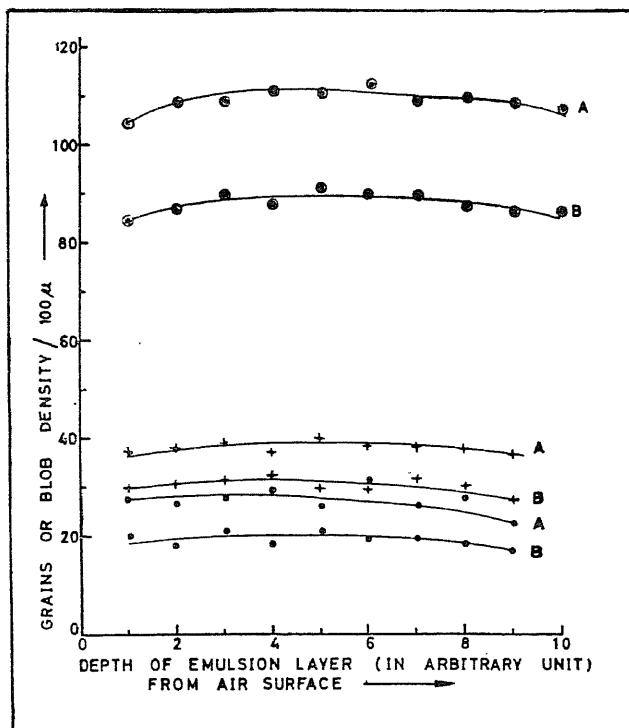


Fig. 5. Variation of Grain and Blob Density with Depth of Emulsion Layer from the Air Surface (Represented in Arbitrary Units) for Relativistic Ω^- Particle and Minimum Ionization Electron Tracks in Stack A and Stack B.
 -○-○-○-Curves are For Ω^- Particles and -●-●-●-Curves for Plateau Ionization Electrons and Both Show the Variation of Grain Density + + + + Curves Show the Variation of Blob Density for Relativistic Ω^- Particle Tracks

The results of mass measurements in these two stacks (A and B) are shown in table 4. The masses of heavy mesons decaying at rest in the emulsions have been determined by three different methods (i) gap length parameter at the end of the track and probability of development at less ionizing regions, (ii) gap density measurements and (iii) the multiple scattering measurements whose details have already been given. By these methods, 11 K-mesons disintegrating at rest (5 examples of τ -mode of decay disintegrating into three charged secondaries and 6 examples of K-modes decaying into a single charged particle) are shown. It is found that the values of the masses of all K-mesons obtained by three different methods are more or less in good agreement, the scattering results being a little higher. The average value of masses of all the K-mesons is obtained as $983 \pm 16m_e$ and the weighted average mass value of Σ -hyperons is found to be equal to $2377 \pm 60m_e$. These results are in agreement with the mass values due to other workers (Powell *et al.*¹⁶).

ACKNOWLEDGEMENTS

The author wishes to express his sincere gratefulness to Prof. P. S. Gill for his continuous help and guidance in this work. He is thankful to Prof. M. G. K. Menon and Dr. R. R. Daniel, T.I.F.R., Bombay for allowing him to work on their emulsion stacks.

REFERENCES

1. Fowler, P. H., *Phil. Mag.*, **41**, 169 (1950).
2. Hodgson, P. E., *Ibid.*, **41**, 725 (1950).
3. Renardier, M., Moucharafieh, H., and Morand, M., *C. R. Acad. Sci.*, **231**, 848 (1950).
4. Renardier, M., and Avignon, Y., *Ibid.*, **233**, 393 (1951).
5. Kayas, G., *Ibid.*, **238**, 2153 (1954), *J. Phys., Rad.*, **15**, 34 (1954).
6. O'Ceallaigh, C., *Bagnères Conf. report*, P. '73 (1953).
7. O'Ceallaigh, C., *C.E.R.N. report, secr. St. Meas.*, No. 11 (1954).
8. Fowler, P. H., and Perkins, D. H., *Phil Mag.*, **46**, 587 (1955).
9. Sharma, A. P., Ph.d. Thesis (Aligarh 1961).
10. Sharma, A. P., and Gill, P. S., *Proc. Cosmic-ray Symposium*, (Ahmedabad 1960), p. 353.
11. Sharma, A. P., and Gill, P. S., *Proc. National Institute of Science of India*, **28**, 166 (1962).
12. Sharma, A. P., and Gill, P. S., *Suppl. Nuovo Cimento*, **26**, 205 (1962).
13. Tsai-Chu, and Claret, J., *C. R. Acad. Sci.*, **244**, 2381 (1957).
14. Fay, H., Gottstein, K., and Hain, K., *Suppl. Nuovo Cimento*, **11**, 234 (1954).
15. Baroni, G., and Castagnoli, C., *Ibid.*, **12**, 364 (1954).
16. Powell, C. F., Fowler, P. H., and Perkins, D. H., *The study of Elementary Particles by the photographic Method*, Pergamon Press, (New York, 1959) pp. 292, 310, 316, and 360.

STUDIES ON THE COAGULATION OF SILVER IODIDE SOL, PART IV

By

S. S. UPPAL

Chemical Laboratories, University of Allahabad, Allahabad

and

S. GHOSH

Chemical Laboratories, University of Jabalpur, Jabalpur

[Received on 28th November, 1963]

ABSTRACT

The stability of lyophobic sols is governed by the mutual electrical repulsion of the colloidal units due to the similarity of the electric charge on them, which they acquire by the preferential adsorption of one type of ions of the electrolyte in which they are suspended. A change of concentration of the peptising electrolyte will result in a variation of the surface potential of the colloidal units and thus the stability of the sol is affected. In this paper, we have studied the effect of the concentration of the peptising electrolyte, potassium iodide, on the stability of the negative silver iodide sol towards its coagulation by the nitrates of potassium, barium and aluminium at three different temperatures. The values of the energy of activation E and the relative values of the steric factor P have been calculated. The factor P and E are found to be related with the state of aggregation and the electric charge of the colloidal particles and are, therefore, important in defining the stability of the sol.

INTRODUCTION

It is well known that the stability of the sols is affected by heat and they usually become more sensitive towards electrolytes on warming. Very few conclusive data, is, however, available in literature on the coagulation of lyophobic sols at different temperatures. Conflicting results were reported earlier by different workers in the setting time of silicic acid and manganous arsenate gels. Hurd and associate (1) for the first time reported the energy of activation for the gelation of silicic acid considering this process as similar to a simple chemical reaction. Ghosh and coworkers (5) have also made similar studies on the gel formation of the silicates of ferric, chromium, calcium, barium, strontium etc., and have recently extended their observations to the lyophobic sols.

In the coagulation of a lyophobic sol by the addition of an electrolyte, the colloidal units aggregate by collisions and the growing particles continue to take part in the process till they grow to a size where their surface forces become very weak and they have grown to lose the Brownian movement resulting in the separation of the colloidal matter as a precipitate. In a chemical reaction the resultants unite to form a product and therefore, they may be eliminated from the process. Thus considering coagulation to be a rate process and therefore, analogous to a chemical reaction, the energy of activation E may be calculated using the equation

$$\log t = - \log KP\zeta + \frac{E}{2.303 RT} \quad (1)$$

where t is the time of coagulation, P the steric factor, ζ the number of collisions per unit time between the particles present in a unit volume, T the absolute temperature and K is a constant.

We have studied the coagulation of negative silver iodide sol peptised with different amounts of potassium iodide at different temperatures using the nitrates of potassium, barium and aluminium as coagulating electrolytes to investigate the influence of the charge density of the colloidal particles on the steric factor P and the energy of activation E .

EXPERIMENTAL

Five samples of the sol were prepared as described in part I (4) with different amounts of potassium iodide. The silver iodide content in each sample was kept 0.016 gram mole per litre and the sols A, B, C, D and E thus prepared contained 0.0012, 0.0020, 0.0040, 0.0060 and 0.0080 gram mole per litre respectively of an excess of potassium iodide solution. Potassium nitrate equivalent to silver nitrate produced in the sol preparation was also present. These samples were kept for 48 hours after which the coagulation values were found to vary only slightly on ageing. The coagulation values of these sols were determined at three temperatures by mixing 2 ml of the sol with definite amount of an electrolyte and distilled water to keep the total volume 10 ml. The time of coagulation t to a particle size which cannot pass through Whatman filter paper No. 44 was determined for the sols. The energy of activation has been determined from the slope of the straight line obtained by plotting the logarithm of the time of coagulation in minutes against the inverse of absolute temperature. The relative values of Z have been calculated by substituting the corresponding values of E , T and t in equation (1). The values of E and those of KPZ obtained as described above are noted in tables I to VI.

TABLE I

KKO_3 gM/l	E in calories for the sols				
	A	B	C	D	E
0.160	5834	5720	5492	5335	5034
0.152	5607	5720	5034	5034	4805
0.144	5492	5262	4919	4691	4576
0.136	4805	4805	4576	4576	4348
0.120	4691	4348	3890	3661	3318

TABLE II

$\text{Ba}(\text{NO}_3)_2$ mgM/l	E in calories for the sols				
	A	B	C	D	E
2.50	6407	6063	5950	5950	6292
2.30	5720	5720	5720	5492	5607
2.10	5034	4919	4691	4691	4691
1.90	4348	4348	4119	4119	4004

TABLE III

Al (NO ₃) ₃ mgM/l	<i>E</i> in calories for the sols				
	A	B	C	D	E
0·0277	5950	5950	6179	6407	5492
0·0267	5607	5492	5492	5720	4691
0·0257	4805	4576	4691	5031	4348
0·0246	4462	4348	4348	4576	3890

TABLE IV

KNO ₃ gM/l	<i>KPZ</i> for the sols				
	A	B	C	D	E
0·160	564·9	406·2	245·5	145·2	178·2
0·152	309·7	274·8	71·6	56·9	66·1
0·144	199·5	88·4	38·7	23·1	31·3
0·136	52·3	29·6	15·6	13·5	16·3
0·120	26·6	6·9	2·2	1·5	1·6

TABLE V

Ba (NO ₃) ₂ mgM/l	<i>KPZ</i> for the sols				
	A	B	C	D	E
2·50	3192·0	1667·0	963·8	659·2	1500·0
2·30	477·5	354·0	228·6	127·4	276·7
2·10	71·6	43·5	19·9	17·5	35·0
1·90	12·6	8·4	3·4	3·6	6·3

TABLE VI

Al (NO ₃) ₃ mgM/l	<i>KPZ</i> for the sols				
	A	B	C	D	E
0·0277	342·0	1227·0	1879·0	3192·0	758·6
0·0267	123·6	350·8	452·0	706·3	121·3
0·0257	17·4	53·1	78·3	175·8	40·8
0·0246	5·9	23·0	30·3	59·6	6·6

DISCUSSION

As a given sol treated by different accounts of an electrolyte flocculates after a certain growth in the size of the colloidal particles, the value of Z for the same sol concentration may be taken as constant. In other words, the variations in the value of KPZ give the relative variations of P . From the results we find that the relative value of P continuously increase with the increasing concentrations of the electrolyte used for coagulation. Similarly, the values of E increase, though not so prominently, with the increasing concentrations of the electrolyte. It is, therefore, concluded that the values of P are related with the residual electric charge on the colloidal particles and the values of E are related with the size of the particles such that it becomes larger for the aggregates of the larger dimensions. It is, therefore, seen from the results that for the same amount of the added electrolyte potassium nitrate and barium nitrate the values of P decrease with increasing concentrations of potassium iodide upto a definite concentration, clearly indicating that the charge on the colloidal particles has increased. With larger amounts of potassium iodide as in the case of the sol E , the value of P increase and it is also observed that it becomes less stable than the sol D towards its coagulation by electrolytes potassium nitrate and barium nitrate. Then when larger amount of potassium iodide is used the coagulating effect of potassium ions from potassium iodide added becomes prominent.

The behaviour of aluminium ions from aluminium nitrate is different throughout as the value of P increases for the sols stabilised with increasing amounts of potassium iodide. Our results clearly show that in all the above cases the sol becomes more stable towards its coagulation by aluminium ions as the charge on the colloidal units is increased by the addition of the increasing concentrations of potassium iodide. This has also been reported by Klompé (2) for the coagulation of negative silver iodide by lanthanum nitrate. According to Kruyt (3) this is due to the coagulating action of trivalent ions as cementing centres between the colloidal silver iodide units and this will be more pronounced the higher the surface potential of the particles.

CONCLUSION

From the results it may be concluded that the theory of the reaction rates is applicable to the process of aggregation and the chief difference between the two is that unlike a chemical reaction, the aggregated particles continue to grow till their surface forces for aggregation die out and the particles become too large to possess effective Brownian movement. It is further shown that the steric factor P decreases with the increasing charge density and E increases with the progressive aggregation of the colloidal particles.

REFERENCES

1. Hurd, C. B. and Larteron, H. A., *J. Phys. Chem.*, 36, 604 (1932).
2. Klompé, M. A. M. and Kruyt, H. R., *Kolloid-Beihufie*, 54, 484 (1942).
3. Kruyt, H. R., *Colloid Science*, Vol. I, p. 310.
4. Uppal, S. S. and Ghosh, S., *Proc. Nat. Acad. Sci., India*, 32A, 368 (1962).
5. Yadava, K. L. and Ghosh, S., *Kolloid-Z.*, 153, 39, 40, 166, 168 (1957); 154, 51, 54 (1957).

AMINO DERIVATIVES OF ZIRCONIUM TETRABROMIDE : PART II

By

SARJU PRASAD and MISS MOMOTA BISWAS

Department of Chemistry, Banaras Hindu University, Varanasi-5

[Received on 19th February, 1964]

ABSTRACT

Compounds of $ZrBr_4$ with some secondary and tertiary amines and heterocyclic bases have been prepared, their properties studied and structures discussed.

INTRODUCTION

In a previous communication¹ amino derivatives of $ZrBr_4$ with mono and diamines were prepared and their properties studied. The work has now been extended to the study of similar compounds with secondary and tertiary amines and heterocyclic bases.

EXPERIMENTAL

$ZrBr_4$ was prepared as described in Part I, extracted with ethyl acetate and filtered. The solution was analysed for purity.

(Found Zr = 22.27% and Br = 78.28% ; Calculated Zr = 22.19% and Br = 77.81%) and used in all the experiments.

A strong ethyl acetate solution of the organic substance was added to the $ZrBr_4$ in ethyl acetate with constant shaking till the precipitation was complete and there was a slight excess of the organic compound. It was filtered and the precipitate washed till the washings did not give any precipitate with $ZrBr_4$ solution. All these operations have been carried out in a dry atmosphere. The precipitate was pressed between the folds of filter paper and finally dried in vacuum desiccator.

Zr was estimated as ZrO_2 , and bromine as AgBr by Piria and Schiff's Method. Nitrogen was estimated either by Kjeldahal's or Dumas' method and the percentage of organic matter calculated from the percentage of nitrogen obtained.

TABLE I
Compounds with Secondary and Tertiary Amines and heterocyclic bases

No.	Amines	Compounds formed	Colour	Zirconium		Bromine %	Nitrogen %	Organic matter %
				Found Calc.	Found Calc.			
1.	Ethyl-aniline	Zr ($C_6H_5NHCH_2H_5)_4 Br_4$	Ash	10·45	10·19	35·55	35·75	6·12
2.	Triethylamine	Zr ($N(C_2H_5)_3)_4 Br_4$	Pinkish white	11·11	11·19	39·50	39·25	6·78
3.	Dimethyl amine	Zr ($C_6H_5N(CH_3)_2)_4 Br_4$	White	9·74	10·19	36·09	35·75	6·16
4.	Diethyl amine	Zr ($C_6H_5N(C_2H_5)_2)_4 Br_4$	Dirty white	10·45	9·06	31·43	31·78	5·50
5.	N-Methyl amine	Zr ($C_6H_5NHCH_3)_4 Br_4$	Dirty white	11·30	10·86	36·91	38·14	6·58
6.	Benzyl amine	Zr ($C_6H_5NHCH_2C_6H_5)_4 Br_4$	White	12·09	11·74	40·78	41·18	3·55
7.	Nicotine	Zr ($C_{10}H_{14}N)_2 Br_4$	Brown	13·84	12·37	42·96	43·51	7·68
8.	Dibenzyl amine	Zr ($C_6H_5N(CH_2C_6H_5)_2)_2 Br_4$	Dirty white	9·62	9·53	33·14	33·44	2·90
9.	p-aminodimethyl aniline	Zr ($C_6H_{12}N_2)_2 Br_4$	Greyish white	12·15	13·36	48·03	46·85	8·02
10.	p-aminodiethyl aniline	Zr ($C_{10}H_{16}N_2)_2 Br_4$	Reddish white	11·62	12·34	44·11	43·30	7·49
11.	Diphenylamine	Zr (($C_6H_5)_2NH)_2 Br_4$	Whitish brown	12·59	12·17	44·11	42·72	3·68
12.	Diphenyl Benzidine	Zr ($C_{24}H_{20}N_2)_2 Br_4$	Whitish brown	8·80	8·42	29·18	29·54	5·11
13.	α -picoline	Zr ($C_6H_7N)_2 Br_4$	Green	15·02	15·28	53·22	53·59	4·61
14.	r-picoline	Zr ($C_6H_7N)_2 Br_4$	Green	15·07	15·28	53·52	53·59	4·75

GENERAL PROPERTIES

Almost all the compounds are coloured, amorphous and fairly stable in dry atmosphere but begin to hydrolyse when left in moist atmosphere for a long time or treated with water, NaOH or Na_2CO_3 solution. They do not give a sharp melting point but decompose when heated. When heated alone in a dry test tube a sublimate deposits in the cooler part of the test tube and responds to the test of amine and bromine but when heated with soda lime the amine sublimes and is deposited on the cooler part of the test tube. They are insoluble or sparingly soluble in benzene, ether and alcohol but fairly soluble in mineral acids. The water extract gives the test for bromine, which shows that probably it is in an ionisable state.

DISCUSSION

An examination of the results shows that by the action of amines on ZrBr_4 two types of compounds are formed. In one, one molecule of ZrBr_4 combines with four molecules of N-methyl aniline, dimethyl aniline, ethyl aniline, diethyl aniline and triethyl aniline.

In the other one molecule of ZrBr_4 combines with two molecules of *p*-amino-dimethyl aniline, *p*-amino-diethyl aniline, diphenyl benzidine, dibenzyl aniline, diphenylamine and benzyl aniline which is probably due to the formation of chelate compounds in the first three cases and due to steric hinderance in the rest.

With heterocyclic bases similar results have been obtained. One molecule of ZrBr_4 combines with two molecules of *α*-picoline, *r*-picoline and nicotine.

In none of these compounds the E. A. N. assumes the inert gas configuration and hence the compounds are not very stable.

The authors' sincere thanks are due to the authorities of the Banaras Hindu University for providing facilities.

REFERENCE

1. S. Prasad and K. Sahney, *Proc. Nat. Acad. Sci., India*, 30A, 307 (1960).

COMPOUNDS OF ZIRCONIUM TETRABROMIDE WITH NITROANILINES, AMINOPHENOLS, AMINOBENZOIC ACIDS, AMIDES ANILIDES etc.

By

SARJU PRASAD and MISS K. SHYAMALA DEVI

Chemical Laboratories, Banaras Hindu University, Varanasi-5

[Received on 15th February, 1964]

ABSTRACT

Compounds of $ZrBr_4$ with nitroanilines, aminophenols, aminobenzoic acids, anilides etc. have been prepared in ethyl acetate medium, their properties studied and probable structures assigned to them.

INTRODUCTION

A general survey of the literature shows that practically no work has been done on the formation of compounds of $ZrBr_4$ with organic substances, in non-aqueous media except in this laboratory^{1,2} when amino derivatives of $ZrBr_4$ have been prepared in ethyl acetate medium and their properties studied.

The present investigation deals with the studies on preparation and properties of the compounds of $ZrBr_4$ with nitroanilines, aminophenols, aminobenzoic acids, amides, anilides, etc.

EXPERIMENTAL

The chemicals used were of B. D. H. or E. Merck's extra pure quality. Ethyl acetate was dehydrated and distilled. Zirconium tetrabromide was prepared as described earlier (*loc. cit.*), extracted with ethyl acetate, filtered and analysed for purity.

Ethyl acetate solution of the organic substance was slowly added to $ZrBr_4$ solution with constant shaking till the precipitation was complete and the organic substance was in slight excess. The precipitate was filtered, washed free of the organic substance with ethyl acetate, dried in a vacuum desiccator over calcium chloride and analysed. Zirconium was estimated as ZrO_2 and bromine as $AgBr$ by Piria and Schiff's method. The organic matter was found by difference.

GENERAL PROPERTIES

All the compounds are insoluble in common organic solvents, stable in dry atmosphere at the room temperature but begin to decompose when they come into contact with the moisture of the atmosphere. All the compounds except that formed with benzamide decompose when heated. The compound formed with benzamide melts at 185°C.

TABLE I

No.	Organic substance	Compound formed	Colour	Zirconium Found %	Zirconium Calc. %	Bromine Found %	Bromine Calc. %	Organic matter % Found	Organic matter % Calc.
1.	<i>o</i> -Nitroaniline	$\text{Zr}(\text{NO}_2\text{C}_6\text{H}_4\text{NH}_2)_4 \text{Br}_4$	Brown	9.27	9.48	33.49	33.19	57.24	57.33
2.	<i>m</i> -Nitroaniline	$\text{Zr}(\text{NO}_2\text{C}_6\text{H}_4\text{NH}_2)_4 \text{Br}_4$ do	Pale yellow	9.07	9.48	33.47	33.19	57.46	57.33
3.	<i>p</i> -Nitroaniline	$\text{Zr}(\text{NO}_2\text{C}_6\text{H}_4\text{NH}_2)_4 \text{Br}_4$ do	Yellow	9.59	9.48	33.34	33.19	57.07	57.33
4.	<i>o</i> -Aminophenol	$\text{Zr}(\text{OH.C}_6\text{H}_4\text{NH}_2)_4 \text{Br}_4$ do	Black	19.24	19.45	34.13	34.07	46.63	46.48
5.	<i>m</i> -Aminophenol	$\text{Zr}(\text{OH.C}_6\text{H}_4\text{NH}_2)_4 \text{Br}_4$ do	Dirty white	19.61	19.45	34.76	34.07	45.63	46.48
6.	<i>p</i> -Aminophenol	$\text{Zr}(\text{OH.C}_6\text{H}_4\text{NH}_2)_4 \text{Br}_4$ do	Dark violet	19.37	19.45	34.78	34.07	45.85	46.48
7.	<i>o</i> -Aminobenzoic acid	$\text{Zr}(\text{COOH.C}_6\text{H}_4\text{NH}_2)_4 \text{Br}_4$ do	Pale yellow	9.52	9.51	33.55	33.33	56.93	57.16
8.	<i>p</i> -Aminobenzoic acid	$\text{Zr}(\text{COOH.C}_6\text{H}_4\text{NH}_2)_4 \text{Br}_4$ do	Yellow	9.09	9.51	33.70	33.33	57.21	57.16
9.	8-Hydroxyquinoline	$\text{Zr}(\text{OH.C}_9\text{H}_6\text{N})_4 \text{Br}_4$	Yellow	9.41	9.20	32.06	32.26	58.53	58.54
10.	2-Aminopyridine	$\text{Zr}(\text{NH}_2\text{C}_6\text{H}_4\text{N})_4 \text{Br}_4$	Orange red	20.19	20.78	36.31	36.40	43.50	42.82
11.	Acetanilide	$\text{Zr}(\text{CH}_3\text{CONH.C}_6\text{H}_5)_4 \text{Br}_4$	Pale yellow	9.73	9.59	33.05	33.61	57.22	56.80
12.	<i>p</i> -Aminoacetanilide	$\text{Zr}(\text{CH}_3\text{CONHC}_6\text{H}_4\text{NH}_2)_4 \text{Br}_4$	Yellow	16.01	16.55	29.38	29.00	54.61	54.45
13.	Benzamide	$\text{Zr}(\text{C}_6\text{H}_5\text{CONH}_2)_4 \text{Br}_4$	White	10.57	10.19	35.94	35.71	53.49	54.10
14.	Benzanilide	$\text{Zr}(\text{C}_6\text{H}_5\text{CONHC}_6\text{H}_5)_4 \text{Br}_4$	White	14.66	14.14	24.65	24.77	60.69	61.09

The aqueous extract of these compounds gives the test for bromine, showing thereby that either bromine is in an ionisable state or the compounds are hydrolysed.

DISCUSSION

An examination of the results shows that one molecule of $ZrBr_4$ combines with 4 or 2 molecules of the organic substance ; the E. A. N. does not assume the inert gas configuration in any of them and hence they are not stable. In the case nitroanilines and amino acids one molecule of $ZrBr_4$ combines with 4 molecules of these substances showing thereby that nitro and carboxylic groups respectively do not co-ordinate in the presence of $-NH_2$ group. Also the compounds of $ZrBr_4$ with acetanilide and benzamide are formed in 1:4 ratio. But it appears that the co-ordination is through carbonyl group as it is much stronger than $-NH_2$ and $=NH$ groups and also due to the greater affinity of Zr for O_2 than for N_2 .

In the case of aminophenols one molecule of $ZrBr_4$ combines with only two molecules of aminophenols showing thereby that both the $-NH_2$ and $-OH$ groups coordinate. Similarly the compounds with aminoacetanilide and 2-aminopyridine are formed in 1:2 ratio. These compounds are comparatively more stable, which may be due to chelation.

In the case of benzanilide one molecule of $ZrBr_4$ combines with only two molecules of the organic compounds, which may be due to steric hinderance.

The authors' sincere thanks are due to the authorities of the Banaras Hindu University for providing the necessary facilities.

REFERENCES

1. S. Prasad and Miss K. Sahney, *Proc. Nat. Acad. Sci., India*, **30A**, 307 (1960).
2. Sarju Prasad and Miss Mamota Biswas, *Proc. Nat. Acad. Sci. (India)* **34A**, 279 (1964).

OXIDIMETRIC DETERMINATION OF THIOUREAS WITH SODIUM VANADATE

By

BALWANT SINGH, BALBIR CHAND VERMA and S. C. NISTANDRA

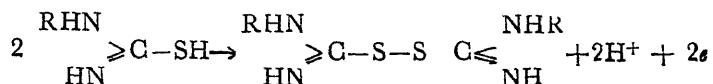
Department of Chemistry, Panjab University, Patiala

[Received on 18th April, 1964]

ABSTRACT

Sodium vanadate has been used as a redox reagent for the indirect oxidimetric determination of thiourea and its organic derivatives in sulphuric acid (6N) medium using iodine monochloride as a catalyst. The excess of vanadate has been determined by titration with ferrous ethylenediamine sulphate (FES) solution.

Thioureas are oxidised to their corresponding disulphides with a single electron change:



(R = hydrogen atom, alkyl or aryl group,

(R = hydrogen atom, alkyl or aryl group)

No attempt seems to have been made so far to estimate thiourea or its organic derivatives with sodium vanadate. In the present investigation an effort has been made to determine thiourea and its many alkyl and aryl derivatives by oxidising them to their corresponding disulphides by an excess of sodium vanadate in sulphuric acid medium and determining the unreacted excess of the oxidant by titration with standard ferrous ethylenediamine sulphate (FES) solution using diphenylbenzidine as an indicator. Singh et al. have shown that thioureas can be quantitatively oxidised to their corresponding disulphides in sulphuric acid medium by potassium iodate¹, iodine monochloride², iodine monobromide³, iodine trichloride⁴, diethylene tetra-ammonium sulphatocerate (DTS)⁵, potassium dichromate⁶ and chloramine-T⁷.

Preliminary experiments show that the reaction between vanadate and thiourea is extremely slow in sulphuric acid medium. The speed of the reaction,

however, increases with an increase in the concentration of sulphuric acid. Iodine monochloride catalyses the reaction. From a number of trial experiments utilising the high acidity of the solution with respect to sulphuric acid and catalytic effect of iodine monochloride, it was found possible to quantitatively oxidise thiourea and its organic derivatives to their corresponding disulphides.

EXPERIMENTAL

Preparation of 0·05 N Sodium Vanadate Solution:

8·50 g. of sodium vanadate were dissolved in hot water containing 1 g. of pure sodium carbonate. The solution was filtered, cooled and its volume made to one litre. It was titrated with standard ferrous ethylenediamine sulphate (FES) solution in sulphuric acid medium using diphenylbenzidine as an indicator, and the vanadate solution was adjusted to the required strength. A standard solution of sodium vanadate prepared in this way was stable for many weeks.

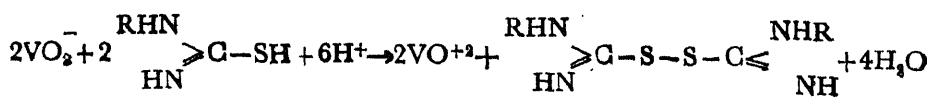
*Procedure:—*A known weight of each compound was taken in a titration flask. In case of thiourea and its alkyl derivatives, sufficient water and enough of sulphuric acid were added to make normality of the solution to 6 N and its volume to 50 to 60 ml. Each aryl derivative was dissolved in 20 ml. of 18 N sulphuric acid and the solution diluted with water (40 ml.) to bring its normality to 6 N. Two to three drops of iodine monochloride (0·02 N) solution were added as catalyst. A known excess of standard (0·05 N) sodium vanadate solution was added to the reaction mixture which was allowed to stand for 5 to 10 minutes to complete the reaction. Water (60 to 70 ml.) and phosphoric acid (5 to 10 ml.) were added and the excess of vanadate was back-titrated with standard (0·05 N) ferrous ethylenediamine sulphate solution using diphenylbenzidine (one or two drops of its one per cent solution in sulphuric acid) as an indicator. The end point (from violet to green) was extremely sharp.

From the volume of standard ferrous ethylenediamine sulphate solution used corresponding to the end point in each titration, the volume of standard sodium vanadate solution used for the oxidation of thiourea and its derivatives was calculated and consequently the amount of thiourea and each of its derivatives was determined. Some typical results are given in the table.

TABLE
Indirect determination of thiourea and its organic derivatives
with standard (0·05N). sodium vanadate

Compound titrated	Weight of the Compound	
	taken g.	found g.
NH ₂ .CS.NH ₂	0·0114	0·0114
	0·0456	0·0457
CH ₃ .NH.CS.NH ₂	0·0132	0·0132
	0·0507	0·0505
CH ₃ CH ₂ NH.CS.NH ₂	0·0143	0·0144
	0·0611	0·0610
(CH ₃) ₂ CHNH.CS.NH ₂	0·0207	0·0207
	0·0664	0·0663
n-CH ₃ CH ₂ CH ₂ CH ₂ NH.CS.NH ₂	0·0241	0·0241
	0·0645	0·0646
(CH ₃) ₂ CHCH ₂ NH.CS.NH ₂	0·0161	0·0162
	0·0618	0·0615
n-CH ₃ CH ₂ CH ₂ CH ₂ CH ₂ NH.CS.NH ₂	0·0149	0·0149
	0·0525	0·0523
O-(CH ₃)C ₆ H ₄ NH.CS.NH ₂	0·0146	0·0145
	0·0627	0·0625
p-(CH ₃)C ₆ H ₄ NH.CS.NH ₂	0·0193	0·0193
	0·0633	0·0630
O-(OCH ₃)C ₆ H ₄ NH.CS.NH ₂	0·0204	0·0203
	0·0649	0·0651
O-(OC ₂ H ₅)C ₆ H ₄ NH.CS.NH ₂	0·0222	0·0222
	0·0554	0·0554

The results recorded in the table show that the listed compounds can be determined indirectly in sulphuric acid medium using sodium vanadate as an oxidant. The oxidation of thiourea and its organic derivatives is represented as:



(R = hydrogen atom, alkyl or aryl group).

ACKNOWLEDGEMENT

One of the authors (B. C. V.) thanks the Council of Scientific and Industrial Research for the award of Senior fellowship.

REFERENCES

1. Singh, B., and B. C. Verma, *Z. analyt. Chem.*, **194**, 112 (1963).
2. Singh, B., B. C. Verma and M. S. Saran, *J. Indian Chem. Soc.*, **39**, 211 (1962).
3. Idem, *Proc. Nat. Acad. Sci. (India)* **33A**, 305 (1969).
4. Idem, *J. Indian Chem. Soc.*, **39**, 490 (1962).
5. Singh, B., and B. C. Verma, *ibid*, **40**, 39 (1963).
6. Idem: *Z. analyt. Chem.*, **196**, 432 (1963).
7. Singh, B., Verma, B. C. and Kalia, Y. K., *J. Indian Chem. Soc.*, **40**, 697 (1963).

STUDIES ON THE EFFECT OF SOIL MOISTURE CONDITIONS AND GIBBERELLIN APPLICATION ON THE NUTRITIVE VALUE OF RICE

By

SANT SINGH and KRISHNA KANT SINGH

College of Agriculture, Banaras Hindu University, Varanasi

[Received on 26th December, 1963]

ABSTRACT

The investigation clearly reveals that adequate supply of soil moisture is essential for the production of nutritive gain in a longer duration variety of paddy. On the whole, 100 p.p.m. concentration of gibberellin has been found highly beneficial in both the cases of soil moisture. Further study has indicated that protein composition is practically unaffected by any of the treatments.

INTRODUCTION

Considerable information about various aspects of the nutritional problem of rice has accumulated during the past three decades or so in our country. However, our knowledge with regard to the effect of soil moisture on the nutritive value is very limited. Mc Garrison (1928) was probably the first worker who studied this problem and tried to throw some light over this important subject.

Gibberellin, which is a plant hormone, generally causes more vegetative growth and early flowering in a number of species (Brian and Grove, 1957). The extent to which its application under different soil moisture conditions during the grain maturation period affects the nutritional value of rice appears to be of great significance particularly when not much information is available on this aspect. Keeping in view the above objective, the present investigation was undertaken during the year 1961 in the College of Agriculture, Banaras Hindu University.

EXPERIMENTAL METHOD

Selection of the Variety, Raising of Seedlings, Transplanting and other Pre-harvest Operations :

A mid duration Variety (T_{21}) well suited to this area was selected and seedlings were raised under the natural conditions of the farm. When they attained the age of 6 weeks, three seedlings of uniform size and appearance were transplanted in the last week of July in each of the puddled cement pots previously filled with well prepared soil according to the procedure laid in the authors' paper (1963). Plants were provided with equal and measured but liberal amount of water and were timely intercultured and dusted with gamaxine. They were allowed to grow till the commencement of grain maturation period i.e., upto the age of 90 days after transplanting and then they were brought inside the glass house so that rain water may not interfere during the course of the experimentation.

Pots were now divided in two sets, one received liberal but equal and measured volume of water till harvesting and was denoted as I_n . In case of the other, after keeping 2" of standing water above the soil surface at the commencement of the period, further supply of irrigation was stopped and the plants were then forced to grow under progressively depleted soil moisture condition. This set

was denoted as I_1 . Following concentrations of gibberellin were sprayed on the plants of each set at an interval of 15 days starting just after the transplanting and continuing till the harvest.

- (i) G_0 - Control, i.e., no spraying of the hormone.
- (ii) G_1 - 25 p.p.m.
- (iii) G_2 - 50 p.p.m.
- (iv) G_3 - 100 p.p.m.

Plots under the following 8 treatment combinations were arranged in a factorial experimental design with three replications :

- (1) $I_n G_0$, (2) $I_n G_1$, (3) $I_n G_2$, (4) $I_n G_3$, (5) $I_1 G_0$, (6) $I_1 G_1$, (7) $I_1 G_2$ and (8) $I_1 G_3$.

Harvesting and Preparation of Grain Samples :

Harvesting of the crop was done when the grains were fully ripened. Grains were then separated from the straw and their husks were removed very carefully. The hulled rice was then ground to a fine powder in an electrically operated micro-grinding mill and the samples were then dried in an electric oven, bottled and sealed.

Chemical Analyses :

Help of Loomis and Shull (1937) was taken for the determination of total carbohydrate and crude protein in the sample. The value of the crude protein was obtained by multiplying the total nitrogen and the factor 6.25. Soxhlet apparatus was used to obtain ether solubles. The period of extraction was 8 hours and the condensation rate was maintained at 4 to 5 drops per second. The extract was then dried for 30 minutes at 100°C, cooled and weighed.

For the detection of various amino acids in the sample, paper chromatographic method, as suggested by Block and Weiss (1956), was used. The chromatogram, developed from each of the hydrolysates, was compared with the standard which was prepared under similar conditions. The help of R_F values as given by Brimley

and Barrett (1956) was also taken in recognising them.

EXPERIMENTAL FINDINGS

A perusal of the accompanying Table clearly illustrates, that in a mid-duration variety, normal irrigation is essential for greater accumulation of the carbohydrate. On the other hand, no marked variation in protein and ether soluble contents due to the two soil moisture conditions was noted.

Effect of gibberellin on the chemical composition of the grain was found to be very spectacular and the nutritive value was increased very appreciably when 100 p.p.m. concentration was used in both the sets of the plants, although the effect was slightly less in the moisture depleted condition.

Further examination of the Table revealed that practically the same amino acids were detected in case of each treatment and hence neither soil moisture nor gibberellin application had got any effect on the protein constituents.

Table Showing the Effect of Soil Moisture Conditions and Gibberellin Application on the Average Chemical Composition (percentage of dry matter) of Rice

Treatment	Total carbohydrate	Ether solubles	Crude protein	Amino acids detected		
(1) I _n G ₀	85.23	2.84	7.13	Alanine (A1), aspartic acid (Asp), cystine (C), glycine (G1), histidine (H), Isoleucine (Isol), lysine (Ly), methionine (M), proline (Pr) and serine (Se).		
(2) I _n G ₁	84.30	2.76	7.22	Same as in the treatment 1.		
(3) I _n G ₂	83.33	2.88	6.65	Apart from other amino acids arginine (A) was also detected.		
(4) I _n G ₃	88.24	3.22	7.53	Same as in the treatment 3.		
(5) I ₁ G ₀	79.00	3.09	7.31	Ditto	Ditto	1.
(6) I ₁ G ₁	76.74	2.59	6.30	Ditto	Ditto	3.
(7) I ₁ G ₂	76.74	2.93	6.74	Ditto	Ditto	1.
(8) I ₁ G ₃	81.52	2.77	7.31	Ditto	Ditto	1.

DISCUSSION

A striking feature of the findings is that progressively depleted soil moisture lowers the carbohydrate content of the grain, whereas the contents of ether solubles and protein are not so much affected. This appears to be quite reasonable in view of the fact that in case of longer duration variety, water requirement is greater than the shorter one and hence with the progressive depletion of soil moisture, the former has to exert increasingly enormous force in drawing and meeting its necessary moisture need. Kramer (1949) has also expressed a similar view. It is quite likely, that a part of the stored energy is utilized for absorption of moisture from increasingly drier soil and the carbohydrate is consumed first, and later on protein and fat are also taken up. Henrici (1944) also found that with dry soil and inhibited photosynthesis there is a constant loss of carbohydrate first and of protein also later on. Kondo *et al* (1941) obtained greater amount of fat and protein in the drought affected grains of rice, but the starch content was appreciably lowered. It is also possible that low status of moisture in the plant might have led to lesser enzymatic activities seated in the protoplasm of leaves and this might have caused reduction in translocation of carbohydrate to the grain.

One of the possible causes of greater accumulation of carbohydrate in the grains of normally irrigated plant might be due to greater supply of nitrogen and also of phosphorous. Kumura (1956) has also reported that during the ripening period of rice, greater synthesis of carbohydrate takes place when the supply of nitrogen and phosphorus is increased.

With regard to the application of gibberellin, it is obvious from the Table that spraying the plant with 100 p.p.m. concentration causes the production of more nutritive grains in the both the sets of moisture conditions. It may be that its application probably increases the rate of photosynthesis (Haber and Tolbert, 1956) and ultimately causes greater accumulation of photosynthetic products in the grain. Increased amount of carbohydrate was also obtained by Thakur and Negi (1959) in sugarcane and Augsten (1961) in *Ficaria verna*.

Nearly the same amino acids have been detected in case of each treatment and therefore it may be said that protein constituents are chiefly controlled by genetical factors.

SUMMARY AND CONCLUSIONS

The present investigation was undertaken to determine the extent to which soil moisture conditions, developed during the grain maturation period and gibberellin application, affect the nutritional quality of the grains of a longer duration variety of paddy. The main findings and conclusions derived are as below :

- (1) Adequate supply of soil moisture is essential for the production of more nutritive grains.
- (2) Application of gibberellin with 100 p.p.m. concentration has been found to be most effective.
- (3) Protein constituents are unaffected by any treatment of soil moisture and gibberellin application.

ACKNOWLEDGEMENT

The authors express their thanks to the University Grants Commission for awarding a scholarship to the junior author. Thanks are also due to the Principal, College of Agriculture, Banaras Hindu University for providing necessary facilities for carrying out the work.

REFERENCES

1. Block, R. J. and Weiss, K. W., "Amino Acid Handbook ; Methods and Results of Protein Analysis". Springfield, Thomas Co. Publication (1956).
2. Brian, P. W. and Grove, J. F., *Endeavour*, 16, 161 (1957).
3. Brimley, R. C. and Barrett, F. C., "Practical Chromatography". Chapman and Hall Ltd., London (1956).
4. Haber, A. H. and Tolbert, N. E., *Plant Physiol.*, 32, 152 (1956).
5. Henrici, M., *Union S. Africa Dept. Agric. and Forest Sci. Bull.*, 256, 1 (1944) ; *Biol. Abst.* 23, 24739.
6. Kondo, M., *Rept. Ohara Agric. Inst. (Japan)*, 32, 504 (1941).
7. Kramer, P. J., "Plant and Soil Water Relationships" McGraw Hill Book Co., Inc. U. S. A. Publication (1949).
8. Kumura, A., *Proc. Crop. Sci. Soc. (Japan)* 24(4), 324 (1956).
9. Loomis, W. E. and Shull, G. A., "Methods in Plant Physiology." McGraw Hill Book Co. Inc. U. S. A. Publication (1937).
10. Mc Garrison, R., *Ind. Jour. Medical Res.*, 15, 915 (1928).
11. Singh, S. and Singh, K. K., *Proc. Nat. Acad. Sci., India*, 33A, 437 (1963).
12. Thakur, C. and Negi, N. S., *Sci. and Cult.*, 24(11), 522 (1959).

ON THE INTEGRALS CONTAINING BESEL'S POLYNOMIALS

By

D. P. BANERJEE

Department of Mathematics, S. V. University, Tirupati (A. P.)

[Received on 10th December, 1963.]

ABSTRACT

In this note Some integrals of the product of Bessel Polynomial and Legendre's Associated functions and Whittakers functions have been found.

The Bessel polynomial satisfies the differential equation

$$x^2 \frac{d^2y}{dx^2} + (2x+2) \frac{dy}{dx} = n(n+1)y$$

which occurs in the theory of travelling spherical waves.

The solution of this [1] is

$$\begin{aligned} y_n &= \sum_{k=0}^n \frac{(n+k)!}{(n-k)! k!} (x/2)^k \\ &= 1 + n(n+1)x/2 + \dots + \frac{(2n)!}{n!} (x/2)^n \end{aligned}$$

In this paper some Integrals have been found using this function.

$$\begin{aligned} \text{We know [2]} \int_0^1 x^\sigma (1-x^2)^{-\mu/2} \cdot p_\nu^\mu(x) dx \\ &= \frac{2^{\mu-1} \left| \frac{1+\sigma}{2}, \sqrt{1+\frac{\sigma}{2}} \right|}{\left| \frac{1+\sigma-\nu-\mu}{2}, \sqrt{\frac{3}{2}+\sigma} - \frac{\nu-\mu}{2} \right|} \quad \text{if } \operatorname{Re} \mu < 1 \\ &\quad \operatorname{Re} \sigma > -1 \end{aligned}$$

Using this and expanding $y_n(2x^2t)$, we have

$$\int_0^1 x^\sigma (1-x^2)^{-\mu/2} \cdot p_\nu^\mu(x) \cdot y_n(2x^2t) dx$$

$$= \frac{2^{\mu-1} \sqrt{\frac{\sigma+1}{2}} \cdot \sqrt{1+\frac{\sigma}{2}}}{\left| 1 + \frac{\sigma-\nu-\mu}{2} \cdot \sqrt{3/2 + \frac{\sigma+\nu-\mu}{2}} \right|} \cdot {}_4F_2 \left[\begin{matrix} n+1, -n, \frac{\sigma+1}{2}, 1+\frac{\sigma}{2} \\ 1 + \frac{\sigma-\nu-\mu}{2}, 3/2 + \frac{\sigma+\nu-\mu}{2}; -t \end{matrix} \right]$$

We know [2] $\int_0^1 x^\sigma (1-x^2)^{m/2} P_\nu^m(x) dx$

$$= \frac{(-1)^m \Gamma_{1/2} + \sigma/2 \cdot \Gamma 1 + \sigma/2 \cdot \Gamma 1 + m + \nu}{2^{m+1} \left| 1 + \sigma/2 + \frac{m-\nu}{2} \cdot \sqrt{3/2 + \sigma/2 + \frac{m+\nu}{2}} \cdot \Gamma 1 - m + \nu \right|} \quad \text{if } \operatorname{Re} \sigma > -1$$

and m is a integer.

Hence $\int_0^1 (1-x^2)^{m/2} x^\sigma p_\nu^m(x) Y_n(2x^2 t) dx$

$$= \frac{(-1)^m \Gamma_{1/2} + \sigma/2 \cdot \Gamma 1 + \sigma/2 \cdot \Gamma 1 + m + \nu}{2^m + 1 \cdot \left| 1 + \sigma/2 + \frac{m-\nu}{2} \cdot \sqrt{3/2 + \sigma/2 + \frac{m+\nu}{2}} \cdot \Gamma 1 - m + \nu \right|} \times {}_4F_2 \left[\begin{matrix} n+1, -n, \frac{1+\sigma}{2}, 1 + \sigma/2; \\ 1 + \sigma/2 + \frac{m-\nu}{2}, 3/2 + \frac{\sigma+m+\nu}{2}; -t \end{matrix} \right] \quad (2)$$

Putting $\mu = \sigma$ in (1) we have $\int_0^1 x^\sigma p_\nu(x) Y_n(2x^2 t) dx$

$$= \frac{\left| \frac{\sigma+1}{2} \cdot \Gamma 1 + \sigma/2 \right|}{2 \left| 1 + \frac{\sigma-\nu}{2} \cdot \sqrt{3/2 + \frac{\sigma+\nu}{2}} \right|} \cdot {}_4F_2 \left[\begin{matrix} n+1, -n, \frac{\sigma+1}{2}, 1 + \sigma/2; \\ 1 + \frac{\sigma-\nu}{2}; 3/2 + \frac{\sigma+\nu}{2}; -t \end{matrix} \right] \quad (3)$$

We know [3] $P_m(z) \cdot P_n(z) = \sum_{r=0}^m \frac{A_{m-r} \cdot A_r \cdot A_{n-r}}{A_{n+m-r}}$

$$\times \left(\frac{2n+2m-4r+1}{2n+2m-2r+1} \right) P_{n+m-2r}^{(z)}$$

where $A_m = \frac{1 \cdot 3 \cdot 5 \dots (2m-1)}{m!}$ if m and n are positive

integers and $m \leq n$.

$$\begin{aligned} \text{Hence } & \int_0^1 x^\sigma \cdot P_m(x) P_n(x) Y_p(2x^2t) dx = \\ & = \sum_{n=0}^m \frac{A_{m-r} \cdot A_r \cdot A_{n-r}}{A_{m+n-r}} \left(\frac{2n+2m-4r+1}{2n+2m-2r+1} \right) \\ & \times \frac{\left[\frac{\sigma+1}{2} \cdot \left[1 + \sigma/2 \right] \right]}{2 \left[1 + \frac{\sigma-n+m+2r}{2}, \frac{3/2 + \sigma+n+m+2r}{2} \right.} \\ & {}_4F_2 \left. \begin{array}{l} n+1, -n, \frac{\sigma+1}{2}, 1+\sigma/2; \\ 1 + \frac{\sigma-n+m+2r}{2}, \frac{3/2 + \sigma+n+m+2r}{2}; \end{array} \right] - t \quad (4) \end{aligned}$$

$$\begin{aligned} \text{We know [4]} & \int_0^\infty x^{l-1} \cdot W_{k,m}(x) \cdot W_{-k,m}(x) dx \\ & = \frac{\Gamma l+1 \cdot \Gamma \frac{1}{2}+m+l/2 \cdot \Gamma \frac{1}{2}-m+l/2}{2 \Gamma 1+k+l/2 \cdot \Gamma 1-k+l/2} \quad \text{if } \operatorname{Re}(l \pm 2m+1) > 0 \\ & \int_0^\infty x^{l-1} \cdot W_{k,m}(x) \cdot W_{-k,m}(x) Y_n(2x^2t) dx \\ & = \sum_{p=0}^n \frac{\frac{l+p}{2}}{\frac{n-p}{2} \cdot \frac{l-p}{2}} \cdot t^p \int_0^\infty x^{l+2p-1} \cdot W_{-k,m}(x) \cdot W_{-k,m}(x) dx \\ & = \sum_{p=0}^n \frac{t^p (n+p)(n+p-1)\dots(n-p+1) \cdot \Gamma l+2p+1}{\frac{1}{2} \left[1+k+\frac{l+2p}{2} \right] \left[1-k+\frac{l+2p}{2} \right]} \\ & \quad \cdot \Gamma \frac{1}{2}+m+\frac{l+2p}{2} \cdot \Gamma \frac{1}{2}-m+\frac{l+2p}{2}. \\ & = \frac{\Gamma l+1 \cdot \Gamma \frac{1}{2}+m+l/2 \cdot \Gamma \frac{1}{2}-m+l/2}{2 \Gamma 1+k+l/2 \cdot \Gamma 1-k+l/2} \cdot \sum_{p=0}^n \frac{t^p}{\frac{1}{2} \left[p \right]} (n+p)\dots(n-p+1) \end{aligned}$$

$$\begin{aligned}
& (l+2p)(l+2p-1)\dots(l+1) \cdot (\tfrac{1}{2}+m+l/2 \times p-1) \dots (\tfrac{1}{2}+m+l/2+1) \cdot (\tfrac{1}{2}-m+l/2+p-1) \\
\times & \frac{\dots(\tfrac{1}{2}+m-l/2+1)}{(1+k+l/2+p-1) \dots (1+k+l/2+1) (1-k+l/2+p-1) \dots (1-k+l/2+1)} \\
= & \frac{\Gamma l+1 \cdot \Gamma \frac{1}{2}+m+l/2 \cdot \Gamma \frac{1}{2}-m+l/2}{2 \Gamma 1+k+l/2 \cdot \Gamma 1-k+l/2} \\
& \times {}_5F_2 \left[\begin{matrix} n+1, -n, \frac{1}{2}+m+l/2, \frac{1}{2}-m+l/2, l/2 \\ 1+k+l/2, 1-k+l/2 \end{matrix} ; -2t \right] \\
\text{if } & (l \pm m+1) > 0 \quad \dots \quad \dots \quad \dots \quad (5)
\end{aligned}$$

REFERENCES

1. Erdelyi (1953). Higher Transcendental Functions, p 172.
2. Erdelyi, *loc. cit.*
3. Whittaker and Watson. Modern Analysis, p. 331.
4. MacRobert T. M. (1942). *Quar. Jour. Math.*, 13-65.

THE CASE OF HYDRO-STATIC PRESSURE IN FINITE DEFORMATION

By

MD. MAHFOOZ ALI SIDDIQUI

Department of Mathematics, Osmania University, Hyderabad-7

[Received on 12th December, 1963]

ABSTRACT

Retaining third degree terms in the strain energy function and using Lame's constant for an isotropic elastic body a non linear stress-strain relation is obtained which, together with the non linear Eulerian strain components, is employed in solving the state of stress characterized by a hydro-static pressure. The result obtained is compared to that obtained by Seth, using a linear stress-strain relation. An expression is obtained suggesting qualitatively an yield-stress-in-compression, which is almost twice as great as the one given by the formula of Seth.

Assuming that the external stress vector acting on any portion of the surface is parallel to the normal to the surface and of magnitude $|p|$, uniformly distributed over the surface, the displacements can be written as

$$u = (1 - r)x, \quad v = (1 - r)y, \quad w = (1 - r)z \quad (1.1)$$

where r is a constant.

The components of strain are

$$\epsilon_{xx} = \epsilon_{yy} = \epsilon_{zz} = \frac{1}{2}(1 - r^2) \text{ using}$$

$$2\epsilon_{ij} = u_{i,j} + u_{j,i} - v_{k,ij} - v_{k,ji} \quad (1.2)$$

The stresses given by $T_{ij} = \lambda(1 - I_1)I_1 + 2[\mu - (\lambda + \mu)I_1]\epsilon_{ij} - 4\mu\epsilon_{ai}\epsilon_{aj}$

$$\text{are : } T_{xx} = T_{yy} = T_{zz} = \frac{3\lambda + 2\mu}{2}(1 - r^2)\{1 - 5/2(1 - r^2)\} \quad (1.3)$$

$$T_{yz} = T_{xz} = T_{xy} = 0$$

The body-stress equations of equilibrium are obviously satisfied identically.

The boundary conditions are given by

$$T_{xx} = T_{yy} = T_{zz} = -p \quad (1.4)$$

where $-p$ is the hydro-static pressure applied.

(1.3) and (1.4) immediately yield

$$\frac{3\lambda + 2\mu}{2}(r^2 - 1) + 5/4(3\lambda - 2\mu)(1 - r^2)^2 = p \quad (1.5)$$

We define k_o to be the 'modified bulk modulus' (the ratio between stress and uniform dilatation), so that

$$K_o = \frac{\frac{3}{3} \lambda + 2 \mu}{3} \left\{ 1 + \frac{5}{2} (r^2 - 1) \right\} \equiv K \left\{ 1 + \frac{5}{2} (r^2 - 1) \right\} \quad (1.6)$$

where $K = \lambda + \frac{2}{3} \mu$ is the usual bulk modulus of the linear theory.

If s is written for the ordinary contraction $\left(s = 1 - \frac{1}{r} \right)$ the relation (1.5) can be rewritten as

$$\frac{3 K_o}{2} \left\{ \frac{1}{(1-s)^2} - 1 \right\} = p \quad (1.7)$$

Seth's formula is

$$\frac{3 K}{2} \left\{ \frac{1}{(1-s)^2} - 1 \right\} = p$$

If v_o and v stand for the initial and final (undeformed and deformed) volumes (1.7) assumes the form

$$\frac{3 K}{2} \left[1 + \frac{5}{2} \left\{ \left(\frac{v_o}{v} \right)^{2/3} - 1 \right\} \right] \left[\left(\frac{v_o}{v} \right)^{2/3} - 1 \right] = p \quad (1.7')$$

The yield-stress-in-compression is readily obtained making $S \rightarrow -\infty$, giving the value $\frac{9}{4} K$

Solving the biquadratic equation (1.5) one easily obtains the following

$$r = \left\{ 1 + \frac{-3 K \pm \sqrt{9 K^2 + 20 p}}{10} \right\}^{1/2} \quad (1.8)$$

The following approximate law also follows from (1.5)

$$p = 3 K \left(S + \frac{13}{2} S^2 + 17 S^3 + \dots \right) \quad (1.9)$$

REFERENCES

1. B. R. Seth "Finite strain in Elastic problem" *Phil. Trans. Roy. Soc. London*, 234 (1935).
2. F. D. Murnaghan "Finite deformation of an Elastic solid" John Wiley (1951)
3. M. A. Siddiqui "Finite Simple Tension" *Proc. Nat. Acad. Sci., India*, 34A, 74 (1964)

SOME RESULTS IN FUNCTIONAL DIFFERENTIAL EQUATIONS

By

V. LAKSHMIKANTHAM*

Department of Mathematics, University of Alberta, Calgary (Canada)

[Received on 19th December, 1963]

ABSTRACT

The study of functional differential equations is reduced to the study of ordinary scalar differential equations. The results cover uniqueness, bounds, on the norm of solutions or approximate solutions, stability and boundedness of solutions of unperturbed and perturbed systems.

1. Many problems concerning the behaviour of solutions of ordinary differential equations can be made to depend on a scalar differential equation. Comparison principle of this type has been widely used. In the methods employed, prior knowledge of solutions is not assumed.

The aim of this note is to study analogous problems of functional differential equations by using a similar approach. The study of functional differential equations is reduced to the study of a scalar differential equation. This makes it possible to extend many known results of ordinary differential equations to functional differential equations. For example, the results cover uniqueness, bounds of the norm of solutions or approximate solutions, stability and boundedness of unperturbed and perturbed systems. The approach is essentially similar to that of our own earlier work [3, 4, 5].

2. Let I denote the interval $0 \leq t < \infty$ and R^n , n -dimensional Euclidean space. For any vector $y \in R^n$, let $\|y\|$ denote any convenient norm in R^n . Let B denote the space of continuous functions from $[-\alpha, 0]$ into R^n , $\alpha > 0$. Let the norm in B be defined by $\|\phi\| = \sup_{-\alpha \leq s \leq 0} \|\phi(s)\|$. B is a Banach space with respect to this norm. Given a continuous function $x(u)$, from $[-\alpha, \infty]$ into R^n , define $x_t \in B$ for $t > t_0 \geq 0$ by $x_t = x(t+s)$, $-\alpha \leq s \leq 0$. With this notation, we may write the functional differential equation

$$(2.1) \quad x'(t) = f(t, x_t),$$

where $f(t, \phi)$ is defined and continuous on $I \times B$ and f maps $I \times B$ into R^n . Here and in what follows, denotes the right hand derivative.

Given an initial function $\phi \in B$ at $t = t_0$, and ϵ -approximate solution of (2.1) is any function $x(t_0, \phi)$ satisfying the following conditions :

- (i) $x(t_0, \phi)$ is defined and continuous on $(t_0 - \alpha, \infty)$;
- (ii) $x_{t_0}(t_0, \phi) = \phi$;
- (iii) The derivative of $x(t_0, \phi)$ at t , $x'(t_0, \phi)(t)$

*Sponsored by the Mathematics Research Center, U. S. Army, Madison, Wisconsin, under Contract No. DA-11-022-ORD-2059.

exists for every t in $I_{t_0} = [t_0, \infty]$ except at most for a countable set s and satisfies

$$(2.2) \quad \|x'(t) - f(t, x_t)\| \leq \varepsilon, \quad (\varepsilon > 0)$$

on the interval $I_{t_0} - s$. In case $\varepsilon = 0$, it is understood that s is empty and $x(t_0, \phi)$ is a solution of (2.1).

Let C denote the space of continuous functions from $[-\alpha, \infty]$ into R^n . We need the sub-spaces defined by

$$(2.3) \quad C_1 = [x, y \in C \mid |x_t - y_t| = \|x(t) - y(t)\|],$$

$$(2.4) \quad C_A = [x, y \in C \mid |x_t - y_t| + |A_t| = \|x(t) - y(t) + A(t)\|],$$

where $A > 0$ is a scalar function continuous and defined on $[-\alpha, \infty]$ and $|x_t - y_t| + |A_t| = \sup_s \|x_t(s) - y_t(s)\| A_t(s)$.

$$-\alpha \leq s \leq 0$$

We shall first deduce an important inequality which corresponds to a well-known inequality in ordinary differential equations [2].

Theorem 1. Let the function $w(t, r) \geq 0$ be defined and continuous for $t \in I$ and $r \geq 0$.

For each $t \in I$ and $x, y \in C_1$, let

$$(2.5) \quad \|x(t) - y(t) + h[f(t, x_t) - f(t, y_t)]\| \leq \|x(t) - y(t)\| + hW(t, \|x(t) - y(t)\|),$$

for all sufficiently small $h > 0$. Let $x(t_0, \phi)$ and $y(t_0, \psi)$ be ε_1 -and ε_2 -approximate solutions of (2.1) with the initial functions ϕ and ψ respectively at $t = t_0$. Then, whenever the initial functions ϕ and ψ satisfy the relation

$$(2.6) \quad |\phi - \psi| \leq r_0,$$

we have the inequality

$$(2.7) \quad \|x(t_0, \phi)(t) - y(t_0, \psi)(t)\| \leq r(t; t_0, r_0), \quad (t \geq t_0),$$

where $r(t; t_0, r_0)$ is the maximal solution of

$$(2.8) \quad r' = W(t, r) + \varepsilon_1 + \varepsilon_2, \quad r(t_0; t_0, r_0) = r_0,$$

existing for all $t \geq t_0$.

Proof: Let $x(t_0, \phi)$ and $y(t_0, \psi)$ be ε_1 -and ε_2 -approximate solutions of (2.1) with the initial functions ϕ and ψ at $t = t_0$ satisfying (2.6). Defining

$$(2.9) \quad m(t) = \|x(t_0, \phi)(t) - y(t_0, \psi)(t)\|,$$

we obtain $|m_{t_0}| = |\phi - \psi| \leq r_0$. To prove the inequality (2.7), let us consider

$$(2.10) \quad r' = W(t, r) + \epsilon_1 + \epsilon_2 + \eta, \quad r(t_0) = r_0,$$

which has solutions $r_\eta(t; t_0, r_0)$ for all sufficiently small $\eta > 0$, existing to the right of t_0 as far as $r(t; t_0, r_0)$ exists. Since it is known [2] that $\lim_{\eta \rightarrow 0^+} r_\eta(t; t_0, r_0) = r(t; t_0, r_0)$

= $r(t; t_0, r_0)$, it is sufficient to prove

$$(2.11) \quad m(t) \leq r_\eta(t; t_0, r_0), \quad (t \geq t_0).$$

If (2.11) is not true, let t_1 be the greatest lower bound of numbers $t > t_0$ for which (2.11) is false. Since the functions $m(t)$ and $r_\eta(t)$ are continuous, it follows that

$$(2.12) \quad (i) \quad m(t) \leq r_\eta(t; t_0, r_0), \quad (t_0 \leq t \leq t_1);$$

$$(ii) \quad m(t_1) = r_\eta(t_1; t_0, r_0), \quad (t = t_1);$$

$$(iii) \quad m(t) > r_\eta(t; t_0, r_0), \quad (t_1 \leq t \leq t_1 + h_1), \quad (h_1 > 0).$$

From (2.8) and (ii), (iii) of (2.12), we obtain

$$(2.13) \quad \limsup_{h \rightarrow 0^+} \frac{1}{h} [m(t_1 + h) - m(t_1)] \geq r'_\eta(t_1; t_0, r_0) = W(t_1, r_\eta(t_1; t_0, r_0)) \\ + \epsilon_1 + \epsilon_2 + \eta.$$

Since $W(t, r)$ is non-negative, the solutions $r_\eta(t; t_0, r_0)$ of (2.8) are non-decreasing as t increases. Hence it follows, from (2.6), (2.9) and (i), (ii) of (2.12), that

$$|m_{t_1}| = \sup_{t_1 - \alpha \leq s \leq t_1} m(s) = m(t_1),$$

which implies that (2.5) holds along the approximate solutions $x(t_0, \phi), y(t_0, \psi)$ for $t = t_1$. In view of (2.9), we have, for small $h > 0$,

$$\begin{aligned} m(t_1 + h) &= \|x(t_0, \phi)(t_1 + h) - y(t_0, \psi)(t_1 + h)\| \leq \|x(t_0, \phi)(t_1 + h) - x(t_0, \phi)(t_1)\| \\ &\quad - hf(t_1, x_{t_1}(t_0, \phi)) + \|y(t_0, \psi)(t_1 + h) - y(t_0, \psi)(t_1) - hf(t_1, y_{t_1}(t_0, \psi))\| \\ &\quad + \|x(t_0, \phi)(t_1) - y(t_0, \psi)(t_1) + h[f(t_1, x_{t_1}(t_0, \phi)) - f(t_1, y_{t_1}(t_0, \psi))]\|. \end{aligned}$$

From this follows the inequality, using (2.2) and (2.5),

$$\limsup_{h \rightarrow 0^+} \frac{1}{h} [m(t_1 + h) - m(t_1)] \leq W(t_1, m(t_1)) + \epsilon_1 + \epsilon_2,$$

which, in view of (2.13), is a contradiction. Hence (2.11) holds and this proves the stated result.

Remark: Taking $W(t, r) = kr$, the inequality (2.7) reduces to

$$\|x(t_0, \phi)(t) - y(t_0, \psi)(t)\| \leq r_0 e^{k(t-t_0)} + \frac{(\varepsilon_1 + \varepsilon_2)}{k} (e^{k(t-t_0)} - 1), \quad (t \geq t_0),$$

where $|\phi - \psi| \leq r_0$ and this corresponds to the well-known inequality referred to above [2].

Theorem 2: Let the function $W(t, r) \geq 0$ be defined and continuous for $t \in I$ and $r \geq 0$. Suppose further that the maximal solution of $\bar{r}' = W(t, r)$, $r(t_0) = 0$, is identically zero. For each $t \in I$ and $x, y \in C_1$, let

$\|x(t) - y(t) + h[f(t, x_{t_0}) - f(t, y_{t_0})]\| \leq \|x(t) - y(t)\| + hW(t, \|x(t) - y(t)\|)$, for all sufficiently small $h > 0$. Then, there is at most one solution of (2.1) with the initial function ϕ at $t = t_0$.

The proof of this uniqueness theorem is closely analogous to that of Theorem 1. We omit the details to the reader.

Remark: Let $x(t_0, \phi), y(t_0, \psi)$ be any two solutions of (2.1) and $W(t, r) = v(t) g(r)$,

where $g(r) > 0$ for $r > 0$. It is easy to obtain $r(t; t_0, r_0)$

$$= H^* [H(r_0) + \int_{t_0}^t v(s) ds],$$

where $H(u) = \int_{u_0}^u [g(r)]^{-1} dr$, $u_0 \geq 0$ and H^* is inverse function of H . Thus

from (2.7) we get an upper bound

$$\|x(t_0, \phi)(t) - y(t_0, \psi)(t)\| \leq H^* [H(r_0) + \int_{t_0}^t v(s) ds]$$

which exists as long as $H(r_0) + \int_{t_0}^t v(s) ds$ is in the domain of H^* . This is an extension of a similar result in [1, 6].

3. Consider another functional differential equation

$$(3.1) \quad y'(t) = g(t, y_t),$$

where $g(t, \phi)$ is continuous and defined on $I \times B$ and g maps $I \times B$ into R^n . We assume that the solutions of (2.1) and (3.1) exist for all $t \geq t_0$. Let $x(t_0, \phi)$ and $y(t_0, \psi)$ be any two solutions of (2.1) and (3.1) respectively with the initial functions ϕ and ψ at $t = t_0$. We list below some conditions for convenience,

(i) For each $\alpha > 0$ and $t_0 \geq 0$, there exists a positive function $\beta(t_0, \alpha)$, continuous in t_0 for each α , satisfying

$$\|x(t_0, \phi)(t) - y(t_0, \psi)(t)\| < \beta(t_0, \alpha), \quad (t \geq t_0),$$

whenever $|\phi - \psi| \leq \alpha$.

(ii) The $\beta(t_0, \alpha)$ in (i) is independent of t_0 .

(iii) For each $\eta > 0$ and $t_0 \geq 0$, there exists a positive function $d(t_0, \eta)$, continuous in t_0 for each η , satisfying

$$\|x(t_0, \phi)(t) - y(t_0, \psi)(t)\| < \eta, \quad (t \geq t_0),$$

whenever $|\phi - \psi| \leq d(t_0, \eta)$.

(iv) The $d(t_0, \eta)$ in (iii) is independent of t_0 .

(v) For each $a > 0$ and $t_0 \geq 0$, there exist positive numbers B and $T(t_0, a)$ satisfying

$$\|x(t_0, \phi)(t) - y(t_0, \psi)(t)\| < B, \quad (t \geq t_0 + T(t_0, a)),$$

whenever $|\phi - \psi| \leq a$

(vi) The $T(t_0, a)$ in (v) is independent of t_0 .

(vii) For each $\varepsilon > 0$, $a > 0$ and $t_0 \geq 0$, there exists a positive number $T(t_0, \varepsilon, a)$ satisfying

$$\|x(t_0, \phi)(t) - y(t_0, \psi)(t)\| < \varepsilon, \quad (t \geq t_0 + T(t_0, \varepsilon, a))$$

whenever $|\phi - \psi| \leq a$.

(viii) The $T(t_0, \varepsilon, a)$ in (vii) is independent of t_0 .

Corresponding to the above conditions, if we say that the scalar differential equation

$$(3.2) \quad r' = W(t, r)$$

where $W(t, r) \geq 0$ is defined and continuous for $t \in I$ and $r > 0$, has the property (is), we mean the following condition:

(is) For each $\alpha > 0$ and $t_0 \geq 0$, there exists a positive function $\beta(t_0, \alpha)$, continuous in t_0 for each α , satisfying $r(t; t_0, r_0) < \beta(t_0, \alpha)$ for $t > t_0$, whenever $r_0 \leq \alpha$.

Here $r(t; t_0, r_0)$ is the maximal solution of (3.2) existing for all $t > t_0$ such that $r(t_0; t_0, r_0) = r_0$. We use similar conditions corresponding to (ii) to (iv) in the sequel.

Theorem 3: Let the scalar differential equation (3.2) satisfy one of the conditions (is), (iis), (iiis), (ivs). For each $t \in I$, $x, y \in C_1$, let

$$\|x(t) - y(t) + h[f(t, x_t) - g(t, y_t)]\| \leq \|x(t) - y(t)\| + hW(t, \|x(t) - y(t)\|),$$

for all sufficiently small $h > 0$. Then, one of the corresponding conditions (i), (ii), (iii) (iv) holds.

Proof: Let $x(t_0, \phi), y(t_0, \psi)$ be any two solutions of (2.1) and (3.1) with the initial functions ϕ, ψ at $t = t_0$. Using an argument similar to that of Theorem 1, one obtains

$$\|x(t_0, \phi)(t) - y(t_0, \psi)(t)\| \leq r(t; t_0, r_0), \quad (t \geq t_0).$$

The stated results follow directly from this, because of assumptions.

Theorem 4: (a) Let the scalar differential equation (3.2) satisfy one of the conditions (is), (iis). For each $t \in I$, $x, y \in C_A$, let

$$(3.3) \quad A(t) \|x(t) - y(t) + h[f(t, x_t) - g(t, y_t)]\| \leq \|x(t) - y(t)\| [A(t) - hD^+A(t)] + hW(t, \|x(t) - y(t)\| A(t)),$$

for all sufficiently small $h > 0$, where $D^+A(t) = \lim_{h \rightarrow 0^+} 1/h [A(t+h) - A(t)]$. Then, if

$A^{-1}(t)$ is bounded as $t \rightarrow \infty$, one of the corresponding conditions (v), (vi) holds.

Proof: Let $x(t_0, \phi)$ and $y(t_0, \psi)$ be any two solutions of (2.1) and (3.1) with the initial functions ϕ and ψ at $t = t_0$. Defining $m(t) = \|x(t_0, \phi)(t) - y(t_0, \psi)(t)\| A(t)$ and proceeding as in the proof of Theorem 1 with necessary modifications, one obtains the inequality corresponding to (2.13)

$$\limsup_{h \rightarrow 0^+} 1/h [m(t_1+h) - m(t_1)] \leq r'_\eta(t_1; t_0, r_0) = W(t_1, r_\eta(t_1; t_0, r_0)) + \eta.$$

It also follows in a similar way that (3.3) holds along the solutions $x(t_0, \phi)$ and $y(t_0, \psi)$ for $t = t_1$. Further, we have, for small $h > 0$,

$$\begin{aligned} m(t_1+h) - m(t_1) &= A(t_1+h) [\|x(t_0, \phi)(t_1) - y(t_0, \psi)(t_1) + h\{f(t_1, x_{t_1}(t_0, \phi)) \\ &\quad - g(t_1, y_{t_1}(t_0, \psi))\}] \\ &\quad + \|e(h)\| - \|x(t_0, \phi)(t_1) - y(t_0, \psi)(t_1)\| A(t_1), \end{aligned}$$

where $\|e(h)\|/h \rightarrow 0$ as $h \rightarrow 0$. Because of (3.3), this reduces to

$$m(t_1+h) - m(t_1) \leq \|x(t_0, \phi)(t_1) - y(t_0, \psi)(t_1)\| [A(t_1+h) - A(t_1)] + hA(t_1+h) A^{-1}(t_1) [W(t_1, m(t_1))] - \|x(t_0, \phi)(t_1) - y(t_0, \psi)(t_1)\| D^+A(t_1) + \|e(h)\|/h,$$

which yields the inequality

$$\limsup_{h \rightarrow 0^+} 1/h [m(t_1+h) - m(t_1)] \leq W(t_1, m(t_1)).$$

Now continuing the rest of the argument of Theorem 1, we obtain

$$\|x(t_0, \phi)(t) - y(t_0, \psi)(t)\| A(t) \leq r(t; t_0, r_0) \quad (t \geq t_0),$$

provided $|\phi - \psi| \leq r_0 |A_{t_0}^{-1}|$, where $|A_{t_0}^{-1}| = \sup_{t_0 - \alpha \leq s \leq t_0} |A_{t_0}^{-1}(s)|$. Since

(3.2) has the property (is), given $\alpha / |A_{t_0}^{-1}| > 0$ and $t_0 > 0$, there exists a $\beta(t_0, \alpha)$ such that $r(t; t_0, r_0) < \beta(t_0, \alpha)$ whenever $r_0 \leq \alpha / |A_{t_0}^{-1}|$. Hence it follows that

$$(3.4) \quad \|x(t_0, \phi)(t) - y(t_0, \psi)(t)\| \leq \beta(t_0, \alpha) A^{-1}(t), \quad (t \geq t_0).$$

As $A^{-1}(t)$ is assumed to be bounded as $t \rightarrow \infty$, the existence of a B and $T(t_0, \alpha)$ follows which implies that the condition (v) holds.

If (3.2) satisfies (iis), $\beta(t_0, \alpha)$ is independent of t_0 and the other statement follows immediately. This completes the proof.

Theorem 5. Let the assumption (a) of Theorem 4 hold. Then, if $A(t) \rightarrow \infty$ as $t \rightarrow \infty$, one of the corresponding conditions (vii), (viii) holds.

Because of the assumed conditions on $A(t)$, the proof is immediate from (3.4) we omit the details.

4. We now extend the preceding results to perturbed systems. Corresponding to (2.1) and (3.1), we consider the systems

$$(4.1) \quad x'(t) = f(t, x_t) + F(t, x_t),$$

$$(4.2) \quad y'(t) = g(t, y_t) + G(t, y_t),$$

where F and G are perturbations. Suppose that for each $t \in I$ and $x, y \in C_1$, the perturbations satisfy the condition

$$(4.3) \quad \|F(t, x_t) - G(t, y_t)\| \leq W(t, \|x(t) - y(t)\|),$$

$W(t, r)$ being the same function defined before.

Theorem 6: Let the scalar differential equation (3.2) satisfy one of the conditions (is), (iis), (iiis), (ivs). For each $t \in I$ and $x, y \in C_1$, let

$$(4.4) \quad \|x(t) - y(t) + h [f(t, x_t) - g(t, y_t)]\| \leq \|x(t) - y(t)\|,$$

for all sufficiently small $h > 0$. Then, one of the corresponding conditions (i), (ii), (iii), (iv) holds for solutions of (4.1) and (4.2).

Proof: Let $x, y \in C_1$. Then, for small $h > 0$,

$$\begin{aligned} & \|x(t) - y(t) + h [f(t, x_t) + F(t, x_t) - g(t, y_t) - F(t, y_t)]\| \\ & \leq \|x(t) - y(t) + h [f(t, x_t) - g(t, y_t)]\| + h \|F(t, x_t) - G(t, y_t)\|, \\ & \leq \|x(t) - y(t)\| + h W(t, \|x(t) - y(t)\|), \end{aligned}$$

because of (4.3) and (4.4). Now following the proof of Theorem 3, it is easy to obtain the stated result.

Suppose now that the perturbations satisfy the condition

$$(4.5) \quad A(t) \|F(t, x_t) - G(t, y_t)\| \leq W(t, \|x(t) - y(t)\| A(t))$$

for each $t \in I$ and $x, y \in C_A$. Then theorems corresponding to 4 and 5 may be stated.

Theorem 7: (a) Let the scalar differential equation (3.2) satisfy one of the conditions (i), (ii). For each $t \in I$ and $x, y \in C_A$, let

$$A(t) \|x(t) - y(t) + h [f(t, x_t) - g(t, y_t)]\| \leq \|x(t) - y(t)\| [A(t) - hD^+ A(t)]$$

for all sufficiently small $h > 0$, $D^+ A(t)$ being as defined before. Then, if $A^{-1}(t)$ is bounded as $t \rightarrow \infty$, one of the corresponding conditions (v), (vi) holds for solutions of (4.1) and (4.2).

Theorem 8: Let the assumption (a) of Theorem 7 hold. Then, if $A(t) \rightarrow \infty$ as $t \rightarrow \infty$, one of the corresponding conditions (vii), (viii) holds for solutions of (4.1) and (4.2).

Since Theorems 7 and 8 can be proved by combining the proofs of Theorems 4, 5, and 6, we have the details.

REFERENCES

1. I. Bihari : A generalization of a lemma of Bellman and its application to uniqueness problems of differential equations. *Acta Math. Sci. Hungar* 7, 81-94 (1956).
2. E. A. Coddington and N. Levinson : Theory of ordinary differential equations (1955). McGraw-Hill, New York. 8.
3. V. Lakshmikantham : On the boundedness of solutions of non-linear differential equations. *Proc. Amer. Math. Soc.* 8, 1044-48 (1957).
4. V. Lakshmikantham : Notes on a variety of problems of differential systems *Arch. Rat. Mech. Analysis*, 10, 119-126 (1962).
5. V. Lakshmikantham : Lyapunov function and a basic inequality in delay-differential equations. *Arch. Rat. Mech. Analysis*, 10, 305-310, (1962).
6. C. E. Langenhop; Bounds on the norm of a solution of a general differential equation: *Proc. Amer Math. Soc.* 11, 795-799. (1960).

A QUANTITATIVE METHOD FOR THE ESTIMATION OF HALOGENS

By

E. M. KURIAN and S. GHOSH

Chemical Laboratories, University of Jabalpur, Jabalpur

[Received on 15th January, 1964]

ABSTRACT

Volumetric estimation of chlorine or bromine by oxalate has been described in this paper. The reaction rate of these halogens with oxalate is fairly fast when the pH of the solution is not below 5. The excess of the oxalate can be titrated by permanganate at the pH 5 to 7, as this reaction is induced by halides or halogens.

The reaction of the halogens, chlorine, bromine and iodine with an organic acid like oxalic is usually not fast. Hence the volumetric estimation of the halogens by oxalic acid is not possible. They are estimated usually iodometrically with a standard sodium thiosulphate. At a definite pH the reaction rate of halogens with oxalic acid is found to be in the following decreasing order : chlorine > bromine > iodine. With increasing pH the rate of the reaction, however, increases but for obvious reasons it cannot be increased beyond pH 7, as the excess alkali reacts with the halogens.

We have devised a method for the volumetric estimation of the halogens by oxalic acid on the basis of the observations that permanganate considerably induces the oxidation of oxalic acid by halogens¹ and that halogens and halides under suitable conditions induce the oxidation of oxalate by potassium permanganate which is ordinarily very slow in neutral and weakly acidic medium (our unpublished results). We find that oxalic-oxalate mixture of pH not below 5 and not above 7 is the most appropriate one for the estimation of chlorine and bromine.

EXPERIMENTAL

All the chemicals used were of A. R. or equivalent grade. A standard solution of sodium oxalate was prepared by weighing out the requisite quantity drying at 105-110°C for two hours, cooling in a dessicator and dissolving in the required quantity of redistilled water containing a few drops of IN-sulphuric acid to reduce the pH to between 5 and 7. An excess of sodium oxalate solution was taken in a ground glass stoppered conical flask and the bromine or chlorine water, standardised with thiosulphate solution was administered from a pipette keeping the delivery tip of the pipette just above the surface of the solution. The yellow colour of bromine discharges instantaneously. The acidity was now increased to about 0·6N with respect to sulphuric acid and the permanganate solution, 90-95% of the required quantity, was administered from a micro burette of least count 0·02 ml. The mixture was warmed to 35 to 40°C and the titration was completed by adding permanganate dropwise until a faint pink colour persists for 30 seconds.

The method, is, however, not possible for the estimation of iodine as the permanganate reacts with iodide, a product of the reaction even at pH 7. More-

over, the induced reaction of oxalate and iodine by permanganate is not very fast and hence not amenable for titration purposes:

TABLE 1
Amount of Bromine in m.gms.

Iodometrically	By Oxalate method	Difference
7.992	7.992	0.00
15.98	15.98	0.00
23.98	23.98	0.00
31.96	31.95	0.01
63.94	63.94	0.00
95.90	95.88	0.02
127.9	127.8	0.1

TABLE 2
Amount of Chlorine in m.gms.

Iodometrically	By Oxalate method	Difference
1.418	1.418	0.00
2.837	2.837	0.00
4.255	4.255	0.00
5.672	5.671	0.002
7.092	7.093	0.001

We have found that the results are reproducible and the above two tables are the representatives of the several estimations that have been carried out.

REFERENCES

1. H. Taube, *J. Amer. Chem. Soc.*, 69, 1418 (1947); also Cf. H. L. Kalra, Doctoral Thesis, Allahabad, (1962.)

ON INTEGRALS ASSOCIATED WITH CERTAIN HYPERGEOMETRIC
FUNCTIONS OF THREE VARIABLES

By

H. M. SRIVASTAVA

Department of Mathematics, University of Jodhpur, Jodhpur

[Received on 31st January, 1964]

ABSTRACT

Integrals of Eulerian type have been obtained for Saran's triple hypergeometric functions F_E , F_P and F_R whose existence was conjectured by Lauricella. Besides, simple double integrals associated with F_S and F_T , which are apparently an improvement over the ones previously given by Saran, have been found out.

Lastly, Chaundy's integral representation for Appell's double hypergeometric function of the fourth type has been deduced from one of the results of this paper, thus showing the feasibility to get Chaundy's integral without making use of the results of Burchnall and Chaundy.

1. INTRODUCTION

Lauricella (5) in the year 1893 conjectured the existence of ten hypergeometric functions of three variables, in addition to F_A , F_B , F_C and F_D defined and studied by him. These ten functions, namely F_E , F_F , F_G , F_K , F_M , F_N , F_P , F_R , F_S and F_T , have been defined by Saran (7). The latter has also given their integral representations except for the functions F_E , F_F and F_R . In §§ 2, 3 and 4 of this paper I have obtained the integrals associated with these three hypergeometric functions of three variables.

It may be mentioned here that my approach to the problem is markedly unlike that of Pandey (6) whose aim has been to express these functions as infinite series involving Appell's function F_4 and then to use its integral representation as given by Chaundy (4). Moreover, the integrals obtained by me are of a simpler type giving much more elegantly the symmetry between various parameters of the said functions as also the regions of integration.

In § 5 I have given simple double integrals for the functions F_S and F_T . These differ from the ones given by Saran (7) as their common region of integration is $0 < u < 1$, $0 < v < 1$, instead of $u > 0$, $v > 0$, $u + v < 1$ as obtained by Saran.

From the result of § 3 I have been able, in the last section, to deduce the integral representation for Appell's function F_4 having x, y for its arguments. The advantage of this method over that of Chaundy (4) lies in the fact that it has not required the assumption of the integral associated with F_4 having $x(1-y), y(1-x)$ for its arguments, as previously given by Burchnall and Chaundy (3).

2. INTEGRAL REPRESENTATION FOR F_E .

The function E_E defined in (7) by the equality

$$F_E(\alpha_1, \alpha_1, \beta_1, \beta_2, \beta_2; \gamma_1, \gamma_2, \gamma_3; x, y, z) = \sum_{m=0}^{\infty} \sum_{n=0}^{\infty} \sum_{p=0}^{\infty} \frac{(\alpha_1, m+n+p)(\beta_1, m)(\beta_2, n+p)}{(1, m)(1, n)(1, p)(\gamma_1, m)(\gamma_2, n)(\gamma_3, p)} x^m y^n z^p,$$

where, as usual, $(\lambda, k) = \frac{\Gamma(\lambda+k)}{\Gamma(\lambda)}$, converges absolutely when $|x| < r$, $|y| < s$

and $|z| < t$ such that $r + (\sqrt{s} + \sqrt{t})^2 = 1$.

We can easily write

$$F_E = \sum_{n=0}^{\infty} \frac{(\alpha_1, n)(\beta_2, n)}{(1, n)(\gamma_2, n)} F_3(\alpha_1 + n; \beta_1, \beta_2 + n; \gamma_1, \gamma_3; x, z) y^n, \text{ and using the relation (1)}$$

$$(2.1) \quad \begin{aligned} & \frac{\Gamma(b) \Gamma(b') \Gamma(c - b) \Gamma(c' - b')}{\Gamma(c) \Gamma(c')} F_2(a; b, b'; c, c'; x, y) \\ &= \int_0^1 \int_0^1 U^{b-1} V^{b'-1} (1-U)^{c-b-1} (1-V)^{c'-b'-1} (1-Ux-Vy)^{-a} dU dV, \end{aligned}$$

$$[R1(c) > R1(b) > 0, R1(c') > R1(b') > 0];$$

we obtain

$$\begin{aligned} & \frac{\Gamma(\beta_1) \Gamma(\beta_2)}{\Gamma(\gamma_1) \Gamma(\gamma_3)} F_E \\ &= \sum_{n=0}^{\infty} \int_0^1 \int_0^1 v^{\beta_1 - 1} w^{\beta_2 - 1} (1-v)^{\gamma_1 - \beta_1 - 1} (1-w)^{\gamma_3 - \beta_2 - 1} \\ & \quad (1-vx-wz)^{-\alpha_1} \times \\ & \quad \times \frac{(\alpha_1, n)(1-\gamma_3+\beta_2, n)}{(1, n)(\gamma_2, n)} \left\{ \frac{-wy}{(1-w)(1-vx-wz)} \right\}^n dv dw, \end{aligned}$$

provided $R1(\gamma_1) > R1(\beta_1) > 0$, $R1(\gamma_3) > R1(\beta_2) > 0$.

But if we take y to be sufficiently small so that

$$\left| \frac{wy}{1-w} \right| \leq \xi', \text{ where } 0 < w < 1,$$

and $|x| \leq \xi$, $|z| \leq \xi''$, then

$$\left| \frac{wy}{(1-w)(1-vx-wz)} \right| \leq \frac{\xi'}{1-(\xi+\xi'')} \\ < 1, \text{ when } \xi + \xi' + \xi'' < 1,$$

Thus, in this domain of x, y, z , the above series in v and w converges uniformly over the region of integration. The order of summation and integration can therefore be reversed and we have

$$\begin{aligned} & \frac{\Gamma(\beta_1) \Gamma(\beta_2) \Gamma(\gamma_1 - \beta_1) \Gamma(\gamma_3 - \beta_2)}{\Gamma(\gamma_1) \Gamma(\gamma_3)} F_E \\ &= \int_0^1 \int_0^1 v^{\beta_1 - 1} w^{\beta_2 - 1} (1-v)^{\gamma_1 - \beta_1 - 1} (1-w)^{\gamma_3 - \beta_2 - 1} (1-vx-wz)^{-\alpha_1} \times \\ & \quad \times {}_2F_1 \left\{ \alpha_1, 1 - \gamma_3 + \beta_2; \gamma_2; - \frac{wy}{(1-w)(1-vx-wz)} \right\} dv dw, \end{aligned}$$

valid if $\operatorname{Re}(\gamma_1) > \operatorname{Re}(\beta_1) > 0$, $\operatorname{Re}(\gamma_3) > \operatorname{Re}(\beta_2) > 0$, $\xi + \xi' + \xi'' < 1$.

Again, using the relation (2)

$$\begin{aligned} (2.2) \quad & \frac{\Gamma(\alpha) \Gamma(\gamma - \alpha)}{\Gamma(\gamma)} {}_2F_1(\alpha, \beta; \gamma; z) \\ &= \int_0^1 u^{\alpha-1} (1-u)^{\gamma-\alpha-1} (1-uz)^{-\beta} du, \\ & \quad [\operatorname{Re}(\gamma) > \operatorname{Re}(\alpha) > 0]; \end{aligned}$$

we finally obtain

$$\begin{aligned} (2.3) \quad & \frac{\Gamma(\alpha_1) \Gamma(\beta_1) \Gamma(\beta_2) \Gamma(\gamma_2 - \alpha_1) \Gamma(\gamma_1 - \beta_1) \Gamma(\gamma_3 - \beta_2)}{\Gamma(\gamma_1) \Gamma(\gamma_2) \Gamma(\gamma_3)} F_E \\ &= \int_0^1 \int_0^1 \int_0^1 u^{\alpha_1 - 1} v^{\beta_1 - 1} w^{\beta_2 - 1} (1-u)^{\gamma_2 - \alpha_1 - 1} (1-v)^{\gamma_1 - \beta_1 - 1} \times \\ & \quad \cdot (1-vx-wz)^{1 - \gamma_3 + \beta_2 - \alpha_1} \times \\ & \quad \times \left\{ (1-vx-wz)(1-w) + uvw \right\}^{\gamma_3 - \beta_2 - 1} du dv dw, \end{aligned}$$

provided $\operatorname{Re}(\gamma_1) > \operatorname{Re}(\beta_1) > 0$, $\operatorname{Re}(\gamma_2) > \operatorname{Re}(\alpha_1) > 0$, $\operatorname{Re}(\gamma_3) > \operatorname{Re}(\beta_2) > 0$, and $\xi' + \xi' + \xi'' < 1$.

3. INTEGRAL ASSOCIATED WITH F_F .

The function

$$F_F(\alpha_1, \alpha_1, \alpha_1, \beta_1, \beta_2, \beta_1; \gamma_1, \gamma_2, \gamma_2; x, y, z)$$

$$= \sum_{m=0}^{\infty} \sum_{n=0}^{\infty} \sum_{p=0}^{\infty} \frac{(\alpha_1, m+n+p)(\beta_1, m+p)(\beta_2, n)}{(1, m)(1, n)(1, p)(\gamma_1, m)(\gamma_2, n+p)} x^m y^n z^p,$$

[$(1-s)(s-t) = rs$]

can be written as

$$F_F = \sum_{m=0}^{\infty} \frac{(\alpha_1, m)(\beta_1, m)}{(1, m)(\gamma_1, m)} F_1(\alpha_1 + m; \beta_2, \beta_1 + m; \gamma_2; y, z) x^m,$$

and using the relation (1)

$$(3.1) \quad \frac{\Gamma(a)}{\Gamma(c)} \frac{\Gamma(c-a)}{\Gamma(c)} F_1(a; b, b'; c; x, y)$$

$$\int_0^1 U^{a-1} (1-U)^{c-a-1} (1-Ux)^{-b} (1-Uy)^{-b'} dU,$$

[$R1(c) > R1(a) > 0$];

we obtain

$$\begin{aligned} & \frac{(\alpha_1)}{\Gamma(\gamma_2)} \frac{\Gamma(\gamma_2 - \alpha_1)}{\Gamma(\gamma_2)} F_F \\ &= \sum_{m=0}^{\infty} \int_0^1 u^{\alpha_1 - 1} (1-u)^{\gamma_2 - \alpha_1 - 1} (1-uy)^{-\beta_2} (1-uz)^{-\beta_1} \times \\ & \quad \times \frac{(\beta_1, m)(1-\gamma_2 + \alpha_1, m)}{(1, m)(\gamma_1, m)} \left\{ \frac{-ux}{(1-u)(1-uz)} \right\}^m du, \end{aligned}$$

valid if $R1(\gamma_2) > R1(\alpha_1) > 0$.

Now, taking x small so that $\left| \frac{ux}{1-u} \right| \leq \eta$, where $0 < u < 1$, and $|z| \leq \eta''$,

we see that the above series is uniformly convergent over the region of integration if $\eta + \eta'' < 1$. On reversing, therefore, the order of summation and integration we get

$$\frac{\Gamma(\alpha_1)}{\Gamma(\gamma_2)} \frac{\Gamma(\gamma_2 - \alpha_1)}{\Gamma(\gamma_2)} F_F$$

$$\int_0^1 u^{\alpha_1 - 1} (1-u)^{\gamma_2 - \beta_1 - 1} (1-uy)^{-\beta_2} (1-uz)^{-\beta_1} \times \\ \times {}_3F_1 \left\{ \begin{matrix} \beta_1, 1-\gamma_2 + \alpha_1; \gamma_1; -\frac{ux}{(1-u)(1-uz)} \end{matrix} \right\} du,$$

and using the integral (2.2) we finally obtain

$$(3.2) \quad \frac{\Gamma(\alpha_1) \Gamma(\beta_1) \Gamma(\gamma_1 - \beta_1) \Gamma(\gamma_2 - \alpha_1)}{\Gamma(\gamma_1) \Gamma(\gamma_2)} F_R = \\ = \int_0^1 \int_0^1 u^{\alpha_1 - 1} v^{\beta_1 - 1} (1-v)^{\gamma_1 - \beta_1 - 1} (1-uy)^{-\beta_2} (1-uz)^{1+\alpha_1 - \beta_1 - \gamma_2} \times \\ \times \left\{ (1-u)(1-uz) + uvx \right\}^{\gamma_2 - \alpha_1 - 1} du dv,$$

provided $\operatorname{Re}(\gamma_1) > \operatorname{Re}(\beta_1) > 0$, $\operatorname{Re}(\gamma_2) > \operatorname{Re}(\alpha_1) > 0$, and $\eta + \eta'' < 1$.

4. INTEGRAL REPRESENTATION FOR F_R .

The function

$$F_R(\alpha_1, \alpha_2, \alpha_1, \beta_1, \beta_2, \beta_1; \gamma_1, \gamma_2, \gamma_3; x, y, z) = \\ = \sum_{m=0}^{\infty} \sum_{n=0}^{\infty} \sum_{p=0}^{\infty} \frac{(\alpha_1, m+p)(\alpha_2, n)(\beta_1, m+p)(\beta_2, n)}{(1, m)(1, n)(1, p)(\gamma_1, m)(\gamma_2, n+p)} x^m y^n z^p \\ [s(1 - \sqrt{r})^2 + t(1 - s) = 0]$$

is expressible as

$$F_R = \sum_{m=0}^{\infty} \frac{(\alpha_1, m)(\beta_1, m)}{(1, m)(\gamma_1, m)} F_3(\alpha_2, \alpha_1 + m; \beta_2, \beta_1 + m; \gamma_2; y, z) x^m.$$

Now, using the relation (1)

$$(4.1) \quad \frac{\Gamma(b) \Gamma(b') \Gamma(c - b - b')}{\Gamma(c)} F_3(a, a'; b, b'; c; x, y) = \\ = \int \int U^{b-1} V^{b'-1} (1-U-V)^c (1-Ux)^{-a} (1-Vy)^{-a'} dU dV,$$

[$\operatorname{Re}(c) > \operatorname{Re}(b+b') > 0$, $\operatorname{Re}(b) > 0$, $\operatorname{Re}(b') > 0$; $U > 0$, $V > 0$, $U + V < 1$];

We get

$$\begin{aligned} & \frac{\Gamma(\beta_1) \Gamma(\beta_2)}{\Gamma(\gamma_2)} \frac{\Gamma(\gamma_2 - \beta_1 - \beta_2)}{\Gamma(\gamma_1)} E_R \\ &= \sum_{m=0}^{\infty} \int \int v^{\beta_1 - 1} w^{\beta_2 - 1} (1 - v - w)^{\gamma_2 - \beta_1 - \beta_2} (1 - vz)^{-\alpha_1} (1 - wy)^{-\alpha_2} \times \\ & \quad \times \frac{(\alpha_1, m)}{(1, m)} \frac{(1 - \gamma_2 + \beta_1 + \beta_2, m)}{(\gamma_1, m)} \left\{ \frac{vx}{(1 - v - w)(1 - vz)} \right\}^m dv dw, \end{aligned}$$

valid if $R1(\gamma_2) > R1(\beta_1 + \beta_2) > 0$, $R1(\beta_1) > 0$, $R1(\beta_2) > 0$, the region of integration being $v > 0, w > 0, v + w < 1$.

The above series is uniformly convergent if $\zeta + \xi'' < 1$, where $\left| \frac{vx}{1 - v - w} \right| \leq \zeta$, x being sufficiently small, $v > 0, w > 0, v + w < 1$, and $|z| \leq \xi''$.

The order of summation and integration can therefore be reversed and we get

$$\begin{aligned} & \frac{\Gamma(\beta_1) \Gamma(\beta_2)}{\Gamma(\gamma_2)} \frac{\Gamma(\gamma_2 - \beta_1 - \beta_2)}{\Gamma(\gamma_1)} F_R \\ &= \int \int v^{\beta_1 - 1} w^{\beta_2 - 1} (1 - v - w)^{\gamma_2 - \beta_1 - \beta_2} (1 - vz)^{-\alpha_1} (1 - wy)^{-\alpha_2} \times \\ & \quad \times {}_2F_1 \left\{ \alpha_1, 1 - \gamma_2 + \beta_1 + \beta_2; \gamma_1; - \frac{vx}{(1 - v - w)(1 - vz)} \right\} dv dw, \end{aligned}$$

which by means of the integral (2.2) yields

$$\begin{aligned} (4.2) \quad & \frac{\Gamma(\alpha_1) \Gamma(\beta_1) \Gamma(\beta_2)}{\Gamma(\gamma_1) \Gamma(\gamma_2)} \frac{\Gamma(\gamma_1 - \alpha_1) \Gamma(\gamma_2 - \beta_1 - \beta_2)}{\Gamma(\gamma_1)} F_R \\ &= \int \int \int u^{\alpha_1 - 1} v^{\beta_1 - 1} w^{\beta_2 - 1} (1 - u)^{\gamma_1 - \alpha_1 - 1} (1 - vz)^{\beta_1 + \beta_2 - \gamma_2 + 1 - \alpha_1} \times \\ & \quad \times (1 - wy)^{-\alpha_2} \times \\ & \quad \times \{ (1 - v - w)(1 - vz) + uvx \}^{\gamma_2 - \beta_1 - \beta_2 - 1} du dv dw, \end{aligned}$$

provided $R1(\gamma_1) > R1(\alpha_1) > 0$, $R1(\gamma_2) > R1(\beta_1 + \beta_2) > 0$, $R1(\beta_1) > 0$, $R1(\beta_2) > 0$; $\zeta + \xi'' < 1$; and the triple integral is taken over the region

$$0 < u < 1, v > 0, w > 0, v + w < 1.$$

5. DOUBLE INTEGRALS ASSOCIATED WITH F_S AND F_T .

The functions

$$F_S(\alpha_1, \alpha_2, \alpha_3, \beta_1, \beta_2, \beta_3; \gamma_1, \gamma_2, \gamma_3; x, y, z)$$

$$= \sum_{m=0}^{\infty} \sum_{n=0}^{\infty} \sum_{p=0}^{\infty} \frac{(\alpha_1, m)(\alpha_2, n+p)(\beta_1, m)(\beta_2, n)\beta_3, p)}{(1, m)(1, n)(1, p)(\gamma_1, m+n+p)} x^m y^n z^p$$

$[r+s=rs, s=t]$

and

$$F_T(\alpha_1, \alpha_2, \alpha_3, \beta_1, \beta_2, \beta_3; \gamma_1, \gamma_2, \gamma_3; x, y, z)$$

$$= \sum_{m=0}^{\infty} \sum_{n=0}^{\infty} \sum_{p=0}^{\infty} \frac{(\alpha_1, m)(\alpha_2, n+p)(\beta_1, m+p)(\beta_2, n)}{(1, m)(1, n)(1, p)(\gamma_1, m+n+p)} x^m y^n z^p$$

$[r+s=rs+t]$

can easily be expressed as

$$F_S = \sum_{m=0}^{\infty} \frac{(\alpha_1, m)(\beta_1, m)}{(1, m)(\gamma_1, m)} F_1(\alpha_2, \beta_2, \beta_3; \gamma_1 + m; y, z) x^m$$

$$\text{and } F_T = \sum_{m=0}^{\infty} \frac{(\alpha_1, m)(\beta_1, m)}{(1, m)(\gamma_1, m)} F_1(\alpha_2, \beta_2, \beta_1 + m; \gamma_1 + m; y, z) x^m$$

respectively.

Thus, using (3.1) and (2.2), we finally get

$$(5.1) \quad \frac{\Gamma(\alpha_1) \Gamma(\alpha_2) \Gamma(\gamma_1 - \alpha_1 - \alpha_2)}{\Gamma(\gamma_1)} F_S$$

$$\int_0^1 \int_0^1 u^{\alpha_1 - 1} v^{\alpha_2 - 1} (1-u)^{\gamma_1 - \alpha_1 - \alpha_2 - 1} (1-v)^{\gamma_1 - \alpha_2 - 1} \times \\ \left\{ 1 - u(1-v)x \right\}^{-\beta_1} (1-vy)^{-\beta_2} (1-vz)^{-\beta_3} du dv,$$

valid if $\operatorname{Re}(\gamma_1) > \operatorname{Re}(\alpha_1 + \alpha_2) > 0, \operatorname{Re}(\alpha_1) > 0, \operatorname{Re}(\alpha_2) > 0;$

and

$$(5.2) \quad \frac{\Gamma(\alpha_1) \Gamma(\alpha_2) \Gamma(\gamma_1 - \alpha_1 - \alpha_2)}{\Gamma(\gamma_1)} F_T$$

$$= \int_0^1 \int_0^1 u^{\alpha_1 - 1} v^{\alpha_2 - 1} (1-u)^{\gamma_1 - \alpha_1 - \alpha_2 - 1} (1-v)^{\gamma_1 - \alpha_2 - 1} \times \\ \times \left\{ 1 - u(1-v)x - vz \right\}^{-\beta_1} (1-vy)^{-\beta_2} du dv,$$

provided $\operatorname{Re}(\gamma_1) > \operatorname{Re}(\alpha_1 + \alpha_2) > 0, \operatorname{Re}(\alpha_1) > 0, \operatorname{Re}(\alpha_2) > 0$, and $|x| \leq \mu, |z| \leq \mu''$ such that $\mu + \mu'' < 1$.

6. AN INTERESTING DEDUCTION.

The hypergeometric function

$$F_F = \sum_{n=0}^{\infty} \frac{(\alpha_1, n)(\beta_2, n)}{(1, n)(\gamma_2, n)} F_4 (\alpha_1 + n; \beta_1; \gamma_1, \gamma_2 + n; x, z) y^n$$

reduces to $F_4 (\alpha_1; \beta_1; \gamma_1, \gamma_2; x, z)$ when $\beta_2 = 0$.

From (3.2), therefore, we have

$$\begin{aligned} & \frac{\Gamma(\alpha) \Gamma(\beta)}{\Gamma(\gamma) \Gamma(\gamma')} \frac{\Gamma(\gamma - \beta)}{\Gamma(\gamma - \alpha)} F_4 (\alpha; \beta; \gamma, \gamma'; x, y) \\ & \int_0^1 \int_0^1 u^{\alpha-1} v^{\beta-1} (1-v)^{\gamma-\beta-1} (1-uy)^{1+\alpha-\beta-\gamma'} \times \\ & \quad \times \left\{ ux + (1-u)(1-uy) \right\}^{\gamma'-\alpha-1} du dv, \end{aligned}$$

which by a suitable change of the variables u, v , and on interchanging α and β yields

$$\begin{aligned} (6.1) \dots & \frac{\Gamma(\alpha) \Gamma(\beta)}{\Gamma(\gamma) \Gamma(\gamma')} \frac{\Gamma(\gamma - \alpha)}{\Gamma(\gamma - \beta)} F_4 (\alpha; \beta; \gamma, \gamma'; x, y) \\ & = \int \int u^{\alpha-1} v^{\beta-1} (1-v+ux)^{\gamma'-\beta-1} (1-u+uy)^{\gamma-\alpha-1} du dv, \end{aligned}$$

provided $R1(\gamma) > R1(\alpha) > 0$, $R1(\gamma') > R1(\beta) > 0$, and the region of integration is given by

$$u > 0, v > 0, 1-v+ux > 0, 1-u+uy > 0.$$

This is the integral obtained by Chaundy (4).

ACKNOWLEDGEMENT

I am thankful to Dr. S. Saran for his interest in the preparation of this paper.

REFERENCES

1. Appell, P., and Kampe de Feriet, J., "Fonctions hypergeometriques et hypersphériques, Polynomes d'Hermite", (Paris: Gauthier-Villars, 1926).
2. Bailey, W. N., "Generalised hypergeometric series" (Cambridge Tract, 1935).
3. Burchall, J. L., and Chaundy, T. W., "Expansions of Appell's double hypergeometric functions I": *Quart. Jour. of Math. (Oxford)*, 11, 249-70 (1940).
4. Chaundy, T. W., "An integral for Appell's hypergeometric function F_4 ": *Ganita*, 5 (1954) 231-5.
5. Lauricella, G., "Sulle funzioni ipergeometriche a più variabili": *Rendiconti Circ. Mat. Palermo*, t. vii, 111-58 (1893).
6. Pandey, R. C., "A note on certain hypergeometric integrals": *Ganita*, 12, 97-104 (1961).
7. Saran, S., "Hypergeometric functions of three variables": *Ganita*, 5, 77-91 (1954).

KINETICS OF OXIDATION OF GLYCOL BY PEROXYDISULPHATE
CATALYSED BY SILVER IONS

By

D. D. MISHRA and S. GHOSH

Department of Chemistry, University of Jabalpur, Jabalpur

[Received on 22nd January, 1964]

ABSTRACT

Oxidation of ethylene glycol can be effected by various oxidants. In this paper the Kinetics of the oxidation of this organic substrate by potassium peroxydisulphate has been investigated. Like several reducing substrates the oxidation of glycol does not proceed with a measurable velocity and hence silver ion has been used here as a catalyst. The rate of oxidation of glycol by peroxydisulphate catalysed by silver ions has been found to increase with the increasing silver ion concentration. The total order of the reaction is one. It is negative but fractional with respect to glycol and one with respect to the oxidant. It is concluded that the order with respect to glycol is zero and that it inhibits its own oxidation. Hydrogen ions have been found to depress the rate of the reaction. The temperature coefficient of the reaction is between 2 and 3 and the average values of the energy of activation and entropy of activation (between the temperature 35°C - 45°C), are 18345 cals and -4.89 E. U. respectively. The final product of the oxidation of this reducing substrates has been recognised to be formaldehyde.

EXPERIMENTAL

The experimental method adopted was the same as has been described in an earlier paper.² Like other oxidations of peroxydisulphate the loss of the oxidant was estimated by the method of Szabo *et al.*³ The results were reproducible and repeatable. The data of one typical experiment has been recorded in the table-1.

In most of the experiments first few constants show variations but the constants are fairly agreeable, with greater progress of the reaction. For the average of these rate constants the first few have been rejected.

TABLE 1

Temp. 35°C

Glycol = 0.8N ; Time (min)	$\text{K}_2\text{S}_2\text{O}_8$ = 0.02M ; Vol. of Hypo (ml)	AgNO_3 = 0.0005M $K/2.303 \times 10^4 (\text{Min}^{-1})$
0	5.00	...
20	4.58	19.05
40	4.28	16.90
60	4.04	15.43
80	3.76	15.48
100	3.52	15.25
120	3.28	15.25
140	3.04	15.44
160	2.82	15.55
180	2.64	15.41
200	2.48	15.27
Average		15.38
$K = 35.42 \times 10^{-4} (\text{min}^{-1})$		

EFFECT OF PEROXYDISULPHATE CONCENTRATION

The first order constants obtained with different concentrations of peroxydisulphate are given below :

TABLE 2

Temp. 35°C

Initial concentration of peroxydisulphate (M)	Value of $K \times 10^4$ Min $^{-1}$
0.01	38.25
0.02	35.42
0.04	29.06

Thus the rate constants tend to decrease with the increase in the initial concentration of peroxydisulphate and this behaviour is similar to our observations for glycerol*. This may be ascribed to the specific inhibitory effect of potassium ions as suggested in the case of glycerol.

EFFECT OF GLYCOL CONCENTRATIONS

In the following table the effect of different concentrations of glycol, on the rate of the reaction at different temperatures is given.

TABLE 3

Temp. 35°C

Initial concentration of Glycol M(N)	Values of $K \times 10^4$, (Min $^{-1}$)
0.6	40.32
0.8	35.42
1.2	30.00
1.6	27.98

It follows from the above observations that the rate constants decrease with the increase in the concentrations of Glycol. It may be concluded that the reaction with respect to glycol is of zero order and further it has high inhibition action on the rate of its own oxidation by peroxydisulphate.

The order of the reaction with respect to glycol is now calculated from table 3 and (the order of the reaction for this reducing substrate is found to be slightly negative varying between -0.3 to -0.4) the results given below show a similar study with different concentrations of the catalyst and at different temperatures,

TABLE 4

Initial concentrations of glycol (N)	Temperature	Average order with respect to glycol
0·8 and 1·6	35°C	-0·36
0·6 and 1·2		
0·8 and 1·6		
0·6 and 1·2	40°C	-0·45
0·8 and 1·6		
0·6 and 1·2	45°C	-0·35

The above table shows that there is no change in the order of the reaction with the increase in the temperature.

EFFECT OF CONCENTRATION OF SILVER NITRATE

The influence of the various concentrations of silver ions on the velocity of the oxidation at different temperatures is tabulated below :

TABLE 5

Initial concentration of (Ag^+ ions) (M)	First order constants $K \times 10^4$ at		
	35°C	40°C	45°C
0·0005	35·42	38·96	76·25
0·001	93·91	137·95	206·55
0·002	243·20	374·20	514·72

The above results show that the catalytic activity of silver ion increases with the increasing concentration of the silver ions but the increase does not bear a linear relationship.

EFFECT OF HYDROGEN ION CONCENTRATION

Different amounts of sulphuric acid have been added in the reaction mixtures to study the effect of hydrogen ions in the oxidation of glycol by peroxydisulphate catalysed by monovalent silver ions. The values of the constants at 35°C are reproduced in the following table.

TABLE 6

Concentration of sulphuric acid (M)	Rate constants $K \times 10^4 (\text{Min}^{-1})$
0·01	19·23
0·02	14·48
0·04	12·16

A perusal of the above table shows that as the concentration of sulphuric acid increases the rate constants decrease. It may be concluded that the hydrogen ions depress the rate of oxidation of glycol by peroxydisulphate in the presence of silver ions.

ENERGY OF ACTIVATION

The values of energy of activation, calculated for different ranges of temperatures in the presence of different concentrations of silver nitrate, are given below :

TABLE 7

Temperature range	Energy of activation in cals mole ⁻¹ at different concentrations of silver nitrate (M)		
	0·0005	0·001	0·002
35°C — 40°C	12370	14680	16440
40°C — 45°C	24320	22160	17860
Average	18345	18420	17150

FREQUENCY FACTOR AND ENTROPY OF ACTIVATION

The frequency factor A , calculated from the average value of energy of activation (18345 cals mole⁻¹) at different temperatures has been given in the following table.

TABLE 8

Temperature	$A \times 10^{-9}$ litres mole ⁻¹ Sec ⁻¹
35°C	1361
40°C	1042
45°C	1138
Average	1180

$$A = 1180 \times 10^9 \text{ litres mole}^{-1} \text{ sec}^{-1}$$

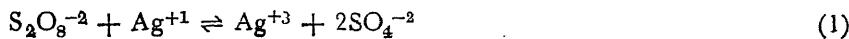
The entropy of activation has been found to be -4·89 E. U.

DISCUSSION

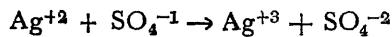
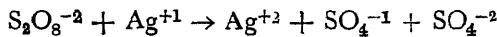
Different workers¹ have suggested various mechanisms for the silver catalysed reduction of peroxydisulphate by the oxidation of different organic and inorganic compounds. In general, the principal steps in the series of these reactions are the interaction between monovalent silver ion and persulphate anion or monovalent silver ion and the radical SO_4^{-1} . Thus for such oxidations involving silver ion as catalyst, the loss of peroxydisulphate may be expressed as

$$-\frac{d [\text{S}_2\text{O}_8^{-2}]}{dt} = K [\text{S}_2\text{O}_8^{-2} [\text{Ag}^+] \text{N}$$

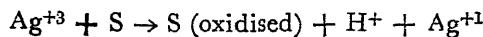
which shows that the expression does not involve the concentration of the reducing substrate and hence the order with respect to it is zero. Our experimental observations show that increasing concentrations of glycol have a depressing effect on the velocity of the reaction. In view of the above consideration we are led to suggest the following mechanism :



The formation of Ag^{+3} in the above reaction may be also shown in two steps as follows :

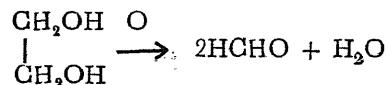


Ag^{+3} so formed in the system reacts with the organic compound and is the rate determining step as has been shown below :—



where S is the organic substance.

The product of the oxidation of glycol has been found to be formaldehyde. It has been confirmed by its usual tests and also by the nature of the melting point of its hydrozone. Our results on the identification of the oxidation products show that during oxidation C-C bond is broken yielding two molecules of formaldehyde.



The negative order obtained in the case of glycol may be explained on the basis that glycol forms a stable complex with Ag^{+3} and thus the amount of Ag^{+3} is lowered and hence the order comes out to be negative.

ACKNOWLEDGMENT

One of the authors (D. D. Mishra) is grateful to Council of Scientific and Industrial Research, New Delhi, for providing a Junior Research fellowship.

REFERENCES

1. (a) Bekier and Kijouski, *Chem. Abstracts*, 30, 3306 (1936).
 (b) Gupta & Ghosh, *J. Indian Chem. Soc.*, 35, 483 (1958); *J. Inorg. Nuclear Chem.*, 9, 17 (1959).
2. D. D. Mishra & Ghosh, Unpublished Work.
3. Szabo *et al*, *Z. anal. Chem.*, 135, 269 (1952).

KINETICS AND MECHANISM OF OXIDATION OF ETHYL ALCOHOL BY QUADRIVALENT CERIUM CATALYSED BY TRIVALENT CHROMIUM

By

JAGDISH PRASAD and SATYESHWAR GHOSH*

Chemical Laboratories, University of Allahabad, Allahabad

[Received on 20th August, 1964]

ABSTRACT

Oxidation of ethyl alcohol by cerium (IV) sulphate is very slow at 30°C but we find that in presence of trivalent chromium the oxidation is sufficiently fast. The reaction was, therefore, studied using trivalent chromium as catalyst. The reaction is of second order i. e. one with respect to ethyl alcohol and one with respect to cerium quadrivalent. The energy of activation of the reaction is 15.08 K. cals and entropy of activation is 27.95 E. U. The mechanism suggested for the reaction is based on the fact that cerium (IV) oxidises trivalent chromium to higher valent stages including hexavalent one which forms unstable ester with ethyl alcohol. Subsequent breaking of this ester gives the final product as acetaldehyde.

EXPERIMENTAL

All chemicals used were that of either A. R. quality or E. Merck or that of the highest purity available.

The solution of ceric sulphate in sulphuric acid was standardised by titration against ferrous ammonium sulphate, N-phenylanthranilic acid being used as indicator. Ethyl alcohol solution was standardised by oxidising it with standard dichromate at boiling point. Chromium chloride solution was standardised by oxidising it to chromate by potassium persulphate.¹ The progress of the reaction was followed as for the reaction between cerium (IV) ion and glycerol.²

The equivalent numbers of cerium (IV) consumed by one mole of ethyl alcohol in presence of chromium chloride were calculated as described for the reaction between cerium (IV) and acetone.³ The average value thus calculated is 2 moles of cerium (IV) for one mole of ethyl alcohol at ordinary temperatures and 12 moles of cerium (IV) for one mole of ethyl alcohol when the mixture was refluxed in presence of chromium chloride. Thus the oxidation is not complete unless the mixture is boiled.

Order of the Reaction: Different concentrations of the reactants ceric sulphate, alcohol, sulphuric acid and chromium chloride were mixed in a precision thermostat and the loss of the oxidant Ce (IV) at different intervals of time was estimated by withdrawing equal parts as described earlier.² In all the reaction mixtures the concentration of alcohol was twelve times or more of that of Ce (IV) and the plots of the logarithms of the concentration of this oxidant at different intervals of time gave a straight line. (Fig 1.) Hence first order constants were calculated with respect to Ce (IV). These were found to be agreeable within the experimental error and the average values are noted in the following table:

*Present Address : Department of Chemistry, University of Jabalpur, Jabalpur.

TABLE I

[Ceric Sulphate] 0·0135M	[Ethyl Alcohol] 0·30M	[Chromium chloride] 0·0047M	[H ₂ SO ₄] 0·4N
Temp	$k' \times 10^2$ (from table)	$k' \times 10^2$ (from fig. 1)	
35°C	1·13	1·13	
40°C	1·80	1·79	
45°C	2·59	2·56	

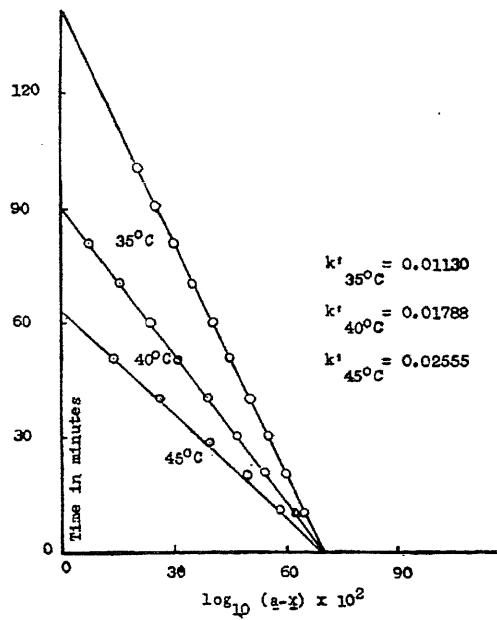


Fig. 1

The order of the reaction with respect to alcohol can be calculated by isolation method and is found to be unity. Hence the total order of the reaction is *two*.

Effect of Sulphuric Acid: Increasing concentration of sulphuric acid increases the rate of the reaction. Initial concentrations of Ce (IV), ethyl alcohol and chromium chloride were kept 0·0135M, 0·30M and 0·004M respectively. Various concentrations of sulphuric acid were added to such reaction mixtures and the results for the average value of the second order rate constants are noted below:

TABLE 2

(H ₂ SO ₄)	$k_s \times 10^2$
0·4N	6·07
0·6N	6·30
0·8N	6·90
1·0N	7·20
1·8N	7·50

It has been generally shown by earlier workers⁴ that the action of sulphuric acid is inhibitory for the oxidations by Ce (IV). The action of sulphuric acid as noted here by us suggests that the oxidation of ethyl alcohol does not proceed through complex formation between cerium (IV) and alcohol but through the formation of an ester between the anion of chromium and alcohol used. This is also confirmed by the action of hydrochloric acid which we find to increase the speed of the reaction. Thus hydrogen ion acts as catalyst for this reaction as reported for the oxidation of hexavalent chromium by several workers.⁵

Effect of chromium chloride: Various concentrations of chromium chloride were added to a mixture containing 0.0135M ceric sulphate, 0.3M ethyl alcohol and 0.4N sulphuric acid. The first order rate constants were found out and are reported in Table 3.

TABLE 3

Temp.	(Chromium chloride)	$k \times 10^2$
40°C	0.000M	Not measurable
do.	0.004M	6.10
do.	0.010M	8.44
do.	0.016M	9.94

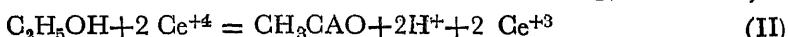
Thus the rate of the reaction is increasing as the concentration of chromium chloride increases.

DISCUSSION

The reaction mechanism suggested here is based on Westheimer's⁵ explanation given for the oxidation of isopropyl alcohol by dichromate through the formation of an ester with the acid anion $\text{HC}_r\text{O}_4^{-1}$. We have noted that at all temperatures of the investigation of the oxidation of ethyl alcohol effected by cerium (IV) sulphate in 0.4N sulphuric acid and in presence of chromium chloride as catalyst, the equivalent number of cerium (IV) consumed by one mole of ethyl is near about two. We have also confirmed that the final oxidised product in this case is acetaldehyde and carbon dioxide is not evolved. Thus the oxidation occurs as suggested below :

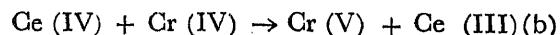
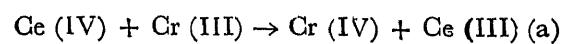


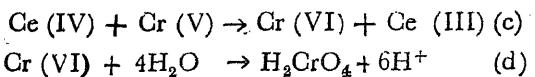
and with cerium (IV) the oxidation may be represented as given below:—



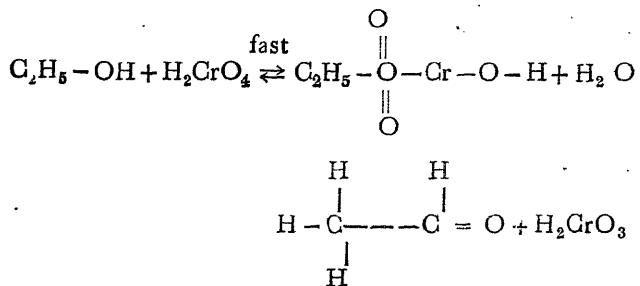
The reaction II will be obviously slow being that of third order.

Addition of chromium chloride enhances the speed of the reaction to a marked extent even at 30°C. This happens because the trivalent chromium is oxidised to hexavalent chromium by cerium (IV). This is possible as cerium (IV) in sulphuric acid medium has an oxidation potential of 1.45 e. v. and hexavalent chromium has an oxidation potential of 1.33 e. v. Thus the above postulation is possible and the mechanism of the oxidation may be cited as below:





H_2CrO_4 acid forms an ester with ethyl alcohol as follows:



Thus the chromium is again reduced to quadrivalent state and the subsequent reactions may be cited as suggested by Westheimer⁵ giving the final product as trivalent chromium. Thus the rate determining step is the decomposition of the ester. The concentration of the ester is proportional to the concentration of ethyl alcohol and the hexavalent chromium which in its turn is proportional to the concentration of trivalent chromium and cerium (IV). The reaction is dependent upon the concentration of cerium (IV) and ethyl alcohol and trivalent chromium.

The mechanism of the reaction is, therefore, simple, i.e. the oxygen is supplied by chromic acid formed by the action of Ce (IV) on trivalent chromium and two hydrogen atoms of ethyl alcohol are removed to form acetaldehyde..

The important fact which is to be mentioned here is that inspite of the fact that the oxidation potential of cerium (IV) in acid is higher than that of hexavalent chromium yet the latter becomes a more active oxidising agent for ethyl alcohol. It is only at higher temperatures (50°C and above) that cerium (IV) alone is capable to oxidise ethyl alcohol. It is also suggested that at higher temperature cerium (IV) reacts with water to produce OH radical so that the reaction mechanism is quite different. It is also necessary to be mentioned that where cerium (IV) is found to form a 1:1 complex with an organic substrate, the oxidation rate is usually fast and measurable even at ordinary temperature as observed by us in case of glycerol oxidation by cerium (IV) alone.²

Thus we conclude that in the present investigation the oxidation of ethyl alcohol by cerium (IV) in presence of trivalent chromium is through the formation of an ester by hexavalent chromium and ethyl alcohol which subsequently decomposes to form acetaldehyde.

REFERENCES

1. A. I. Vogel, Quantitative Inorganic analysis, Second Edition, Longmans, page 297, 70.
2. J. Prasad and S. Ghosh, *Proc. Natl. Acad. Sci. India*, 22A, 159 (1962).
3. J. Shorter and C. Hinshelwood, *J. Chem. Soc.*, 3277 (1950).
4. Littler and W. A. Waters, *Ibid.*, 2767, (1960).
5. F. H. Westheimer, *Chem Rev.*, 45, 419 (1948).

PULSATIONS OF A VISCOUS COMPRESSIBLE FLUID CONFIGURATION

By

P. K. BHATIA and R. S. KUSHWAHA

Department of Mathematics, University of Jodhpur, Jodhpur (Rajasthan)

[Received on 22nd November, 1963]

ABSTRACT

An integral formula for σ^2 , the square of the frequency of oscillations, has been obtained for a viscous compressible fluid configuration in which a magnetic field prevails. It contains an additional term due to the presence of both viscosity and compressibility besides the terms due to their separate effects. The modification due to rigid body rotation on this expression is also obtained.

1. INTRODUCTION

Chandrasekhar (1961) has obtained an integral formula for σ^2 for an incompressible inviscid fluid configuration in which a magnetic field prevails. He further extended the study to include the separate effects of compressibility and viscosity. It was shown that a variational treatment of the problem is possible in the incompressible (inviscid) and compressible cases.

The present paper deals with the combined effects of viscosity and compressibility. An integral formula has been obtained. This differs, from the formula obtained by superposing the two effects obtained separately, in having an additional term.

In the case of compressible fluid this term may be connected with the attenuation of sound in gases. In this case besides viscosity the attenuation also takes place due to heat conduction. But here no attempt is made to show the relative quantitative importance of the two as the latter mode is not considered.

2. FORMULATION OF THE PROBLEM

Consider a viscous compressible fluid configuration confined in a volume V bounded by a surface S . Suppose that in the stationary state a magnetic field prevails and the electrical conductivity is infinite. The space surrounding the fluid, whether finite or infinite, is assumed to be a vacuum. The superscripts 'in' and 'ex' denote the variables pertaining to the interior and exterior of V .

The equations which must be satisfied inside V in the stationary state are

$$(1) \quad \frac{\partial II}{\partial x_i} = \frac{1}{4\pi} \frac{\partial}{\partial x_k} H_i H_k ,$$

where

$$(2) \quad II = p + \frac{\vec{H} \cdot \vec{H}}{8\pi} ,$$

$$(3) \quad P_{ij} = - \left(p + \frac{\vec{H} \cdot \vec{H}}{8\pi} \right) \delta_{ij} + p_{ij} ,$$

and

$$(4) \quad P_{ij} = \mu \left(\frac{\partial U_i}{\partial x_j} + \frac{\partial U_j}{\partial x_i} \right) - \frac{2}{3} \mu \frac{\partial U_k}{\partial x_k} \delta_{ij}.$$

where P_{ij} is the viscous stress tensor and is zero in the stationary state.

The field outside V must be current free and must satisfy the condition

$$(5) \quad \text{Curl } \vec{H} = 0.$$

The continuity of normal stress across the boundary gives,

$$(6) \quad p = \delta_{ij} \left(p + \frac{|\vec{H}|^2}{8\pi} \right) = - \left(\frac{|\vec{H}|^2}{8\pi} \right) \delta_{ij}.$$

In the following analysis, we shall restrict ourselves to the case when

$$(7) \quad \vec{H} \cdot \vec{ds} = 0, \text{ everywhere on } S.$$

This implies that the lines of force of the magnetic field lie on the surface. This is necessary to avoid infinite accelerations on the surface.

The first order perturbations of the initial state are governed by the equations,

$$(8) \quad \rho \frac{\partial U_i}{\partial t} = - \frac{\partial \omega_{ij}}{\partial x_j} + \frac{1}{4\pi} \frac{\partial}{\partial x_i} (H_j h_i + h_j H_i),$$

$$(9) \quad \frac{\partial h_i}{\partial t} = \frac{\partial}{\partial x_j} (H_j U_i - U_j H_i)$$

where \vec{h} denotes the perturbation in the field and

$$(10) \quad \omega_{ij} = \bar{\omega} \delta_{ij} - p_{ij}, \quad \bar{\omega} = \delta_p + \frac{1}{4\pi} H_j h_j.$$

Defining the displacement $\vec{\xi}$ by the relation

$$(11) \quad U_i = \frac{\partial \xi_i}{\partial t},$$

and substituting it in equation (9) and integrating w. r. to t , we get

$$(12) \quad h_i = \frac{\partial}{\partial x_j} (H_j \xi_i - \xi_j H_i).$$

Let us assume that all the quantities describing the perturbed state have the time dependence of the form $e^{i\sigma t}$.

Then equation of motion (8) gives

$$(13) \quad \sigma^2 \rho \xi_i = \frac{\partial \omega_{ij}}{\partial x_j} - \frac{1}{4\pi} \frac{\partial}{\partial x_j} \cdot (H_j h_i + h_j H_i).$$

The perturbation in the field outside V (i. e. in $V^{(ex)}$) satisfies,

$$(14) \quad \text{Curl } \vec{h}^{(ex)} = 0 \text{ and } \text{Curl } \vec{E}^{(ex)} = -i \sigma \vec{h}^{(ex)}.$$

The boundary conditions, which must be satisfied on the displaced boundary $S + \delta S$, are

$$(15) \quad N_i \Delta(P_{ij}) = 0,$$

$$(16) \quad \vec{N} \cdot \vec{H} = 0,$$

$$(17) \quad \vec{N} \times \vec{\Delta}(E) = (\vec{N} \cdot \vec{U}) \vec{\Delta}(H) = i \sigma (\vec{N} \cdot \vec{\xi}) \vec{\Delta}(H),$$

where $\Delta(f)$ denotes the jump that a quantity f experiences on $S + \delta S$ and \vec{N} is the unit outward normal to this surface. Equation (15) ensures the continuity of the normal component of the total stress tensor on the deformed surface.

Equation (16) ensures the vanishing of the normal component of \vec{H} and (17) is derived from the relation

$$(18) \quad \vec{E} + \vec{U} \times \vec{H} = 0.$$

In applying the conditions (15)-(17) one reduces them to conditions on the unperturbed surface S by expanding all the quantities consistently to the first order.

Equations (13)-(14) and boundary conditions (15) to (17) form a characteristic value problem for σ^2 . If $\sigma^{(\lambda)}$ denotes a characteristic value then the solution belonging to it will be distinguished by the same superscript.

If we consider equation (13) belonging to the characteristic value $\sigma^{(\lambda)}$, multiply by $\xi_i^{(\mu)}$ (belonging to a different characteristic value $\sigma^{(\mu)}$) and integrate over the volume V occupied by the fluid, we get

$$(19) \quad (\sigma^{(\lambda)})^2 \int_V \rho \xi_i^{(\lambda)} \xi_i^{(\mu)} dV = \int_V \frac{\partial}{\partial x_j} (\omega_{ij}^{(\lambda)}) \xi_i^{(\mu)} dV$$

$$- \frac{1}{4\pi} \int_V H_j \frac{\partial h_i^{(\lambda)}}{\partial x_j} \xi_i^{(\mu)} dV - \frac{1}{4\pi} \int_V h_j^{(\lambda)} \frac{\partial H_i}{\partial x_j} \xi_i^{(\mu)} dV.$$

$$= I_1 + I_2 + I_3.$$

Integrating I_1 by parts and making use of (10), we get

$$(20) \quad I_1 = \int_S \omega_{ij}^{(\lambda)} \xi_i^{(\mu)} dS_j - \int_V \left(\delta p^{(\lambda)} + \frac{H_k h_k}{4\pi} \right) \frac{\partial \xi_i^{(\mu)}}{\partial x_i} dV \\ + \int_V p_{ij}^{(\lambda)} \frac{\partial \xi_i^{(\mu)}}{\partial x_j} dV.$$

Now $(p_{ij})_S$ is zero. Therefore the surface integral in (20) reduces to

$$(21) \quad \int_S \bar{\omega}_{ij}^{(\lambda)} \xi_i^{(\mu)} dS_i$$

The value of the surface integral (21) is given by (Chandrasekhar)

$$(22) \quad \int_S \bar{\omega}_{ij}^{(\lambda)} \xi_i^{(\mu)} dS_i = \int_S \left(\overset{\rightarrow(o)}{N} \cdot \overset{\rightarrow(\lambda)}{\xi} \right) \left(\overset{\rightarrow(o)}{N} \cdot \overset{\rightarrow(\mu)}{\xi} \right) \\ \left[\overset{\rightarrow(o)}{N} \cdot \text{grad } \Delta_s \text{ (II)} \right] \\ + \frac{1}{4\pi} \int_V h_i^{(\lambda)} h_i^{(\mu)} dV,$$

in which $\Delta_s(f)$ now denotes the jump which a quantity f experiences on S and $\overset{\rightarrow(o)}{N}$ is the unit outward normal to S .

Further we assume that the motion takes place adiabatically so that in the Eulerian framework, this means

$$(23) \quad \frac{\partial}{\partial t} \delta p + U_j \frac{\partial p}{\partial x_j} = \frac{\gamma p}{\rho} \left(\frac{\partial}{\partial t} \delta \rho + U_j \frac{\partial \rho}{\partial x_j} \right),$$

where γ is the ratio of specific heats. The equation of continuity is given by

$$(24) \quad \frac{\partial}{\partial t} \delta \rho + U_j \frac{\partial \rho}{\partial x_j} = - \rho \frac{\partial U_j}{\partial x_j}.$$

Substituting (24) in (23), using (11) and integrating we get δp . Inserting $\delta p^{(\lambda)}$ and \vec{h} from (12), I_1 reduces to

$$\begin{aligned}
I_1 = & \int_S \left(\vec{N} \cdot \vec{\xi}^{(\mu)} \right) \left(\vec{N} \cdot \vec{\xi}^{(\mu)} \right) \left[\vec{N} \cdot \text{grad } \Delta_s \text{ (II)} \right] \\
& + \frac{1}{4\pi} \int_V \overset{(ex)}{h_i^{(\lambda)}} \cdot \overset{(\mu)}{h_i^{(\mu)}} dV \\
(25) \quad & + \int_V \left(c^2 \rho + \frac{|\vec{H}|^2}{4\pi} \right) \frac{\partial \xi_j^{(\lambda)}}{\partial x_j} \cdot \frac{\partial \xi_i^{(\mu)}}{\partial x_i} dV + \\
& + \frac{1}{4\pi} \int_V \left(H_k \frac{\partial H_j}{\partial x_k} \xi_j^{(\lambda)} - H_j H_k \frac{\partial \xi_k^{(\lambda)}}{\partial x_j} \right) \frac{\partial \xi_i^{(\mu)}}{\partial x_i} dV + \\
& \rho v \int_V \left(\frac{\partial \xi_i^{(\lambda)}}{\partial x_j} + \frac{\partial \xi_j^{(\lambda)}}{\partial x_i} \right) \cdot \frac{\partial \xi_i^{(\mu)}}{\partial x_j} dV \\
& - \frac{2}{3} \rho v i \sigma \lambda \int_{(in)} \frac{\partial \xi_k^{(\mu)}}{\partial x_k} \cdot \frac{\partial \xi_i^{(\mu)}}{\partial x_i} dV,
\end{aligned}$$

where s denotes the velocity of sound.

Integrating I_2 by parts, we get

$$(26) \quad I_2 = \frac{1}{4\pi} \int_V H_j \overset{(\lambda)}{h_i} \frac{\partial \xi_i^{(\mu)}}{\partial x_j} dV - \frac{1}{4\pi} \int_S H_j \overset{(\lambda)}{h_i} \overset{(\mu)}{\xi_i} dS_j.$$

In (26), the surface integral vanishes because of (7). Combining the volume integral with I_3 , substituting for \vec{h} from (12) and simplifying, we get

$$\begin{aligned}
(27) \quad J_1 = & \frac{1}{4\pi} \int_V \left(H_k \frac{\partial \xi_i^{(\lambda)}}{\partial x_k} \right) \left(H_j \frac{\partial \xi_i^{(\mu)}}{\partial x_j} \right) dV \\
& + \frac{1}{4\pi} \int_V \frac{\partial \xi_i^{(\lambda)}}{\partial x_i} \left(H_k \frac{\partial H_j}{\partial x_k} \xi_j^{(\mu)} - H_j H_k \frac{\partial \xi_k^{(\mu)}}{\partial x_j} \right) dV
\end{aligned}$$

$$+ \int_V \xi_k^{(\lambda)} \xi_i^{(\mu)} \frac{\partial^2 \Pi}{\partial x_i \partial x_k} dV .$$

Thus we see that equation (19) reduces to

$$(28) \quad (\sigma^{(\lambda)})^2 \int_V \rho \xi_i^{(\lambda)} \xi_i^{(\mu)} dV = I_1 + J_1 ,$$

where I_1 , J_1 are given by (25) and (27)

This is the integral formula which gives the frequency of oscillations for the viscous compressible case. It is easily seen that last term in (25) is present only if both viscosity and compressibility are present. This additional term may be connected with the attenuation of sound in gases.

3. ROTATING FLUID CONFIGURATION

For the case of the same fluid configuration rotating with a uniform angular velocity Ω , the following terms are added to the right hand side of equation (8)

$$2\rho \varepsilon_{ijm} U_j \Omega_m + \rho (\Omega^2 \xi_i - \Omega_i \Omega_j \xi_j)$$

Proceeding as in section 2, we see that the integral formula in this case consists of the following additional terms on the right of (28).

$$\begin{aligned} & \int_V^{(in)} \Omega^2 \rho \xi_i^{(\lambda)} \xi_i^{(\mu)} dV - \int_V^{(in)} \rho \Omega_i \Omega_j \xi_j^{(\lambda)} \xi_i^{(\mu)} dV \\ & + 2i \sigma^{(\lambda)} \int_V^{(in)} \varepsilon_{ijm} \Omega_m \xi_j^{(\lambda)} \xi_i^{(\mu)} dV . \end{aligned}$$

It is easily seen that the effect of rotation is independent of the other effects and it is simply superposable on the other cases.

ACKNOWLEDGEMENTS

One of the authors (P. K. B.) gratefully thanks the University Grants Commission, India for the award of a fellowship.

REFERENCES

Chandrasekhar, S., Hydrodynamic and Hydromagnetic stability. (Oxford, Clarendon Press)
Chapter XIV, Secs. 122 and 123. (1961).

THERMOGRAVIMETRIC ANALYSIS OF SOME PLANT GUMS

By

VIRENDRA KUMAR SRIVASTAVA and RAMA SHANKER RAI*

Chemical Laboratories, University of Gorakhpur, Gorakhpur

[Received on 13th December, 1963]

ABSTRACT

Differential Thermogravimetric Analysis for the first time has been utilized for the identification and characterization of Gum Karaya (*Sterculia Urens*), Gum Dhawa (*Anogeissus latifolia Wall*) and Gum Neem (*Azadirachta Indica*), and their degraded products. D.T.G. curves of the gums and their acids provide a rapid means of their identification and characterization.

Recently Differential Thermal Analysis has been utilized for the characterization of complex organic molecules and a large number of naturally occurring highly polymeric materials like starch and related polysaccharides (8,9). The pyrolysis of highly cross-linked polymers yield thermograms, which are characteristics of natural polymers. Since endothermic breaking and exothermic forming of bonds occur simultaneously in the pyrolysis of substances, it might be possible that endothermic peak be occluded by exothermic peaks arising from oxidation (1,6). Changes in the specific heats and thermal conductivity of polymer during pyrolysis also complicate the picture. However, Differential Thermogravimetric Analysis is not subject to the above mentioned complications. Differential thermal features shown by many natural polymers depend upon chemical composition and macromolecular configuration. It determines the temperature at which changes due to a physical or chemical reaction takes place during the pyrolysis of the substance. The changes may be due to dehydration, transition from one crystalline form to another, destruction of the crystalline lattice, and oxidation decomposition, etc. These changes, their nature and intensity taking place at particular temperatures, are the characteristics of the particular substance.

Several empirical tests have been developed for the identification of gums and polysaccharides (5). All plant gums are complex branched polysaccharides and at present little is known about the spatial arrangement, nature of chains and their fine structures. Studies are confined to the methylated degraded gums and the hydrolysis of methylated gums. This sometimes leads to the possibility of the formation of a new compound or removal of some constituent unit during degradation and hydrolysis. We have first applied the D.T.G. technique for the identification of the following gums and their acids :

1. Gum Karaya or *Sterculia Urens*
2. Gum Dhawa or *Anogeissus latifolia Wall*
3. Gum Neem or *Azadirachta Indica*

The degraded products present in the gum are the gum acid, constituent acid, constituent sugars and sugar acids. Since the plant gums differ in their chemical structures and the constituents present therein, the heat treatment will be different for such of them and D.T.G. provides a rapid means of their identification and characterization.

* Present address : On sabbatical leave to the Department of Chemistry, Washington University, St. Louis 30, Mo., U. S. A.

EXPERIMENTAL

Purification of gums : The native gum, containing bark and leaves of plants and dust, etc., as impurity, was dissolved by keeping in contact with water for 24 hours. As the filtration or decantation is not possible, the impurity was removed by centrifuging at a low speed for a longer time. A dilute solution was prepared and alcohol was added in several steps and the entire mass was shaken until no precipitate settled down. The precipitated mass is white and granular when first formed, but gradually changes to a sticky mass, which could not be suspended again in the supernatant liquid. This indicates that the maximum amount of the gum has been precipitated out. The inodules were dried in vacuum at about 100°C and were made to a coarse powder.

Preparation of the gum acids : (i) *Gum karaya or Gum Sterculia Urens* : The procedure is already reported (11).

(ii) *Gum Dhawa or Gum Anogissus latifolia Wall* : The gum was dissolved in warm water and swelling took place initially, but almost complete dissolution took place after keeping for overnight in sufficient quantity of water. The highly viscous solution was filtered through a linen cloth and the filtrate was poured into ethanol, which contained about 1 N HCl solution. This was stirred vigorously, when the gum precipitated out. The precipitated gum was ground with absolute alcohol, and was again dissolved in water. The procedure was repeated thrice until no positive test for chloride ions was given out. The purified mass was dried under vacuum.

(iii) *Gum Melia Azadirachta (Neem)* : The gum was dissolved in cold water and gave a light brown viscous solution. The solution was acidified with one normal hydrochloric acid and was poured into 95% alcohol, with constant stirring. The precipitated gum was filtered, washed successively with ethanol and ether, and dried in vacuum over phosphorous pentoxide. The process was repeated thrice and a white powder was obtained.

All the gums were tested for the sulfate and phosphate anions. Sulfate was found absent, but phosphate was present in traces (0.1%) only.

Thermogravimetric Analysis of Gums and their degraded products : A Stanton Automatic Recording Thermogravimetric Balance was used. A weighed quantity was taken in a silica crucible and was heated with a constant rise of temperature (250°C/hour), and loss in weight with the continuous rise in temperature was recorded on a calibrated graphical chart supplied by the manufacturers (Stanton Instrument Ltd.). The loss due to buoyancy was obtained by heating an empty crucible from room temperature to 800°C. The weights of the samples were plotted on a calibrated graphical chart against the temperature of heating and it is given in the Figure 4. These may be called 'Decomposition Curves'. The data have been used for plotting the differential thermal graphs (D.T.G.) by recording the loss in weight per five minutes against the temperature of the heating. These results are given in the Figures 1-3.

RESULTS

Gum Melia Azadirachta and Azadirachtic Acid : The maximum peak in the D.T.G. study of the gum (Fig. 1) occurs at 360°C, which is due to the removal of the structural (OH) groups. The other peak at 560°C represents the complete decomposition of the gum.

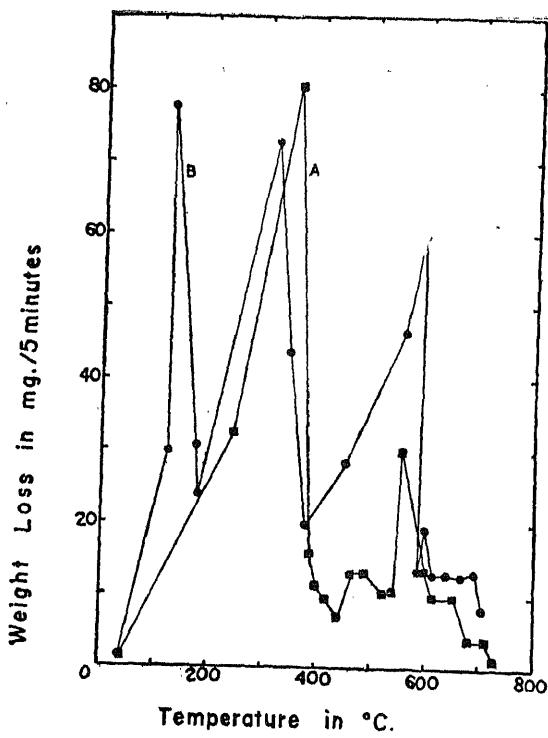


Figure 1. D. T. G. record for the gum *Azadirachta Indica* ex T. G. record (curve A); *Azadirachtic Acid* ex T. G. record (B)

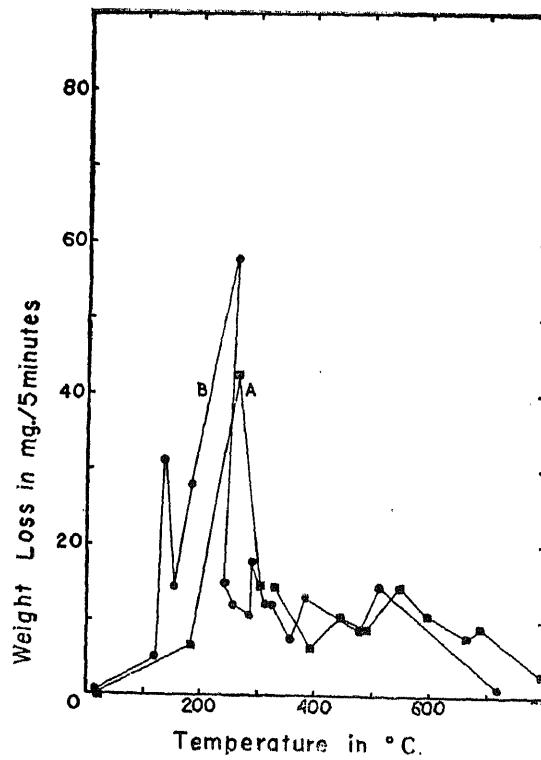


Figure 2. D. T. G. record for Gum *Anogeissus latifolia* Wall ex T. G. record (curve A); *Anogeissus latifolic Acid* ex T. G. record (B)

The gum acid (Fig. 1) gives four peaks at 110° , 280° , 590° , and 600°C respectively. The increase in the number of the peaks is due to the fact that the gum units on hydrolysis are converted into more free constituent units. On heating, water molecules adhered to the gum acid, are removed at 110°C . The peak at 280°C is due to the removal of glucuronic acid and the peak at 590°C is probably due to α -d-glucose. Decomposition takes place at 600°C .

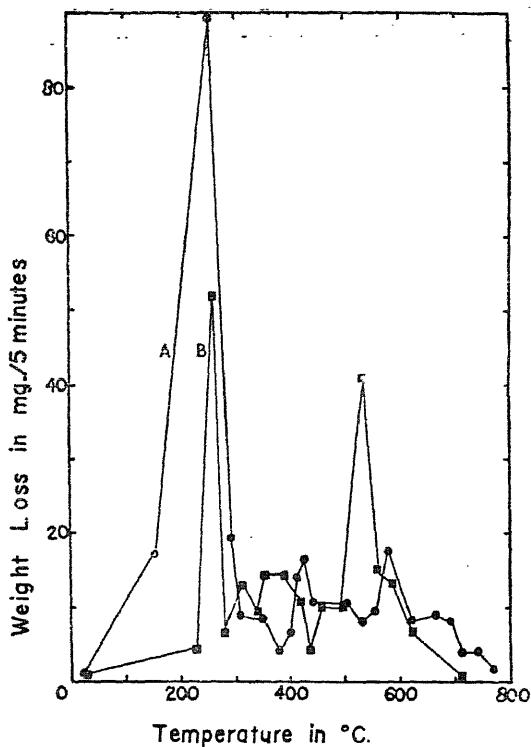


Figure 3. D. T. G. record for Gum Sterculia Urens ex T. G. record (curve A); Sterculia Urenic Acid ex T. G. record (B)

The decomposition curves of the gum and gum acid are given in the Fig. 4. In the former case the first stage of the decomposition appears to be complete at 140°C . Beyond this point the loss is mainly due to the removal of the (OH) groups and complete decomposition takes place at about 700°C . In the case of the gum acid the first stage of the decomposition appears to be complete at 120°C , which is due to the d-galactose (main residue, m.p. 120°C). Complete decomposition takes at 690°C .

Cum Dhawa or Anogeissus latifolia Wall and Anogeissus latifolia Acid : D.T.G. study of the gum (Fig. 2) shows a maximum peak at 270°C , which is due to the removal of the structural (OH) groups. There are two other smaller peaks at 450°C , and 560°C , which arise mainly due to the rearrangement in the structure itself. Complete decomposition of the gum takes places at 690°C .

D. T. G. curve of the gum acid shows more peaks. Here our results are in agreement with the previous workers, who using other analytical techniques found

that methylated gum Ghatti on hydrolysis gives additional products, than methylated degraded gum ghatti (2, 3, 7). The first peak at 110°C is due to the removal of the water molecules. The structural (OH) groups are removed at 240°C . The peak at 290° and 380°C arise due to the internal rearrangement, and complete decomposition takes place at 510°C . The first stage of the decomposition of the gum (Fig. 4) appears to be complete at about 180°C . Beyond this point the loss is mainly due to the removal of (OH) groups and the decomposition is complete at about 770°C . The first stage of the decomposition of the gum acid (Fig. 4) appears to be complete at 125°C and complete decomposition takes place at 725°C .

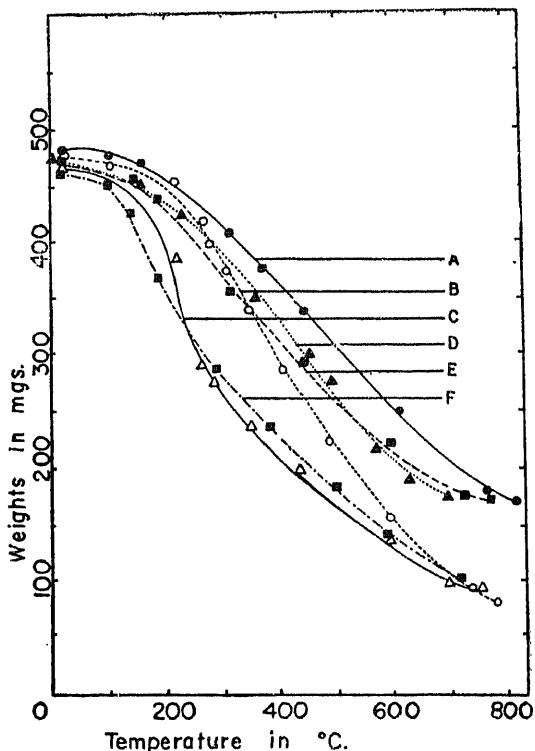


Figure 4. Decomposition Curves for the Gums and Gum Acids.
 Gum Azadirachta Indica (A)
 Azadirachtic Acid (B)
 Gum Anogeissus latifolia Wall (C)
 Anogeissus latifolic Acid (D)
 Gum Sterculia Urens (E)
 Sterculia Urenic Acid (F)

Gum Sterculia Urens or Gum Karaya and Sterculia Urenic Acid : The results obtained by previous workers, using different analytical techniques, differ considerably for the different constituent units (4, 10). Therefore present observation might be useful in the identification and characterization of the gum and gum acid. D.T.G. curves of the gum (Fig. 3) shows a maximum peak at 270°C which is due to the removal of the structural (OH) groups from the gum. The peak at 310°C and a

minimum peak at 440°C are due to the structural rearrangement and complete decomposition takes place at 535°C .

The gum acid (Fig. 3) gives out peak at 260°C , which is due to the removal of the structural (OH) groups. Two other peaks are observed at 430°C and 590°C .

The decomposition curves of the gum and gum acid are given in the Figure 4. The first stage of the decomposition of the gum appears to be complete at about 160°C . Beyond this point the loss is mainly due to the removal of the (OH) groups and complete decomposition takes place at 705°C . The first stage of the decomposition of the gum acid was complete at about 160° and complete decomposition takes place at 675°C .

One of the authors (V.K.S.) is thankful to the Ministry of Education, Government of India for the award of a fellowship during the tenure of this work. Thanks are also due to the Scientific Research Committee, U. P., India, for the grant for this equipment.

REFERENCES

1. Anderson, H. C., *Nature* 191, 1088 (1961).
2. Aspinall, G. O, Hirst, E. L., and Wickstrom, A., *J. Am. Chem. Soc.*, 1160 (1955).
3. Hanna, D., and Shaw, Jr., E. H., *Proc. S. Dakota Acad. Sci.* 27, 78 (1941).
4. Hirst, E. L., and Dunston, Sonia, *J. Chem. Soc.* 2332 (1933).
5. Hirst, E. L., and Jones, J. K. N., "In Modern Methods of Plant Analysis", Vol. II, ed. K. Paech and M. V. Tracey, p. 275, Springer-Verlag, Berlin (1955).
6. Mitchell, B. D., *Sci. Proc. Roy. Dublin Soc.* A1, 105 (1960).
7. Montgomery, R. and Smith, F., *J. Amer. Chem. Soc.* 3225 (1955).
8. Morita, H., *Anal. Chem.* 28, 64 (1956); *J. Amer. Chem. Soc.* 1397 (1955).
9. Morita, H., and Rice, H. M., *Anal. Chem.* 27, 336 (1955).
10. Rao, P. S., and Sharma, R. K., *Proc. Indian Acad. Sci.* 45A, 24 (1957).
11. Srivastava, V. K., and Rai, R. S., *Indian J. Appl. Chem.* 25, 33 (1962).

COLLOIDAL PROPERTIES OF GUM MELIA AZADIRACHTA (NEÉM)

By

VIRENDRA KUMAR SRIVASTAVA and RAMA SHANKER RAI*

Chemical Laboratories, University of Gorakhpur, Gorakhpur

[Received on 13th December, 1963]

ABSTRACT

Electrometric titration curves of a solution of the gum Melia Azadirachta with KOH and Ba(OH)₂ are identical. They demonstrate that the combination with alkali takes place in equivalent proportion. The results with HCl indicate that the gum acid is not amphoteric. The curve relating the conductance of the volume of solution that contains one gram of the gum acid and the square root of concentration decreases linearly at lower concentrations, but two kinds are obtained at higher concentrations, which are due to aggregate formation. The interaction of the gum solution with non-electrolytes show either an increase or decrease in the pH. These changes do not follow a definite order. The relative viscosity versus concentration curve is non-linear at lower concentrations. But at higher concentrations, it rises rapidly. The relative viscosity increases slowly upto pH 7.5, by the addition of sodium hydroxide. Beyond this point it shoots up with a kink, attains a maximum value at pH 10.6 and then falls off rapidly. Such variations almost attain a steady state beyond pH 11.5. These results show that the gum is a polyelectrolyte, and behaves as a lyophilic colloid. On the addition of an increasing amount of methyl alcohol to the gum solution, the specific viscosity rises at low concentrations, attains a maximum value and falls off rapidly. It becomes almost stationary beyond a certain limit. All the viscosity changes are explained by the folding chain theory, aggregate formation, and hydration of the polyelectrolyte units.

INTRODUCTION

The gums in general are known as biocolloids for a long time. It has been shown that gum arabic is molecularly dispersed in water and the colloidal chemical properties are due to the colloidal dimensions of the molecules.¹ Previous investigations have indicated that plant gums behave as polyelectrolytes.² Despite considerable industrial use of the viscous character of solutions of gums, only a few have been studied from a physico-chemical point of view. Since a number of synthetic polyelectrolytes have been studied³ and a number of correlations between observed physical properties and chain structures have been deduced and verified, therefore, it was thought to extend these studies to gum melia azadirachta in order to obtain some information.

The gum is obtained as an exudate from a tropical tree known as Azadirachta Indica. The gum is a neutral salt of a complex polysaccharide acid and is found in pale yellow to light brown nodules. Complete hydrolysis of the gum followed by, partition chromatography, and the separation of the crystalline derivative, has shown that the gum contains L-arabinose, L-fucose, D-galactose, D-glucuronic acid, and traces of D-xylose. The ratio of D-galactose to L-arabinose proved to be 3:2. The gum acid obtained on precipitation of the gum from an acidified aqueous solution with alcohol has an equivalent weight of 1080.⁴

EXPERIMENTAL

Purification of the gum : The native gum contains impurity in the form of bark and leaves of the plant and dust etc. The gum was dissolved in water. As decantation or filtration is not possible, the impurity was removed by centrifuging at a

*On sabbatical leave to the Department of Chemistry, Washington University St. Louis 30, Missouri, U. S. A.

slow speed for a longer time. Then a dilute solution was prepared and alcohol was added to it. A sticky mass was obtained.

Preparation of the gum solution: The purified gum was dissolved in cold water and gave a light brown viscous solution. The gum acid was precipitated by pouring the solution of the gum, acidified with hydrochloride acid, into 95% alcohol, with constant stirring. The precipitated gum was filtered, washed successively with ethanol and ether, and dried in vacuo over phosphorous pentoxide. The process was repeated thrice, and the white powder was dissolved in water to make a solution.

Analysis of Sulphate and Phosphate: The purified gum was analysed for sulphur and phosphorous, with the expectation that the gum might contain sulphate or phosphate anions, which could account for the acidity of the solutions. The presence of sulphur was ruled out on the evidence that fusion with sodium and subsequent application of sodium nitroprusside and methylene blue gave a negative test. The negative results were also confirmed by fusion with sodium carbonate and Potassium nitrate, and subsequent test for barium sulphate. The presence of phosphate was determined by fusion with sodium carbonate and potassium nitrate and finally treatment with sodium molybdate solution. There is very little phosphorous (0.1%), which is not sufficient to account for the acidity. Matthews⁵ is of the opinion that gums always contain phosphoric acid, which it is impossible to separate entirely from the organic matter without hydrolysis. Phosphoric acid appears to be in union with the gum molecule and it is not impossible that it plays an important part in the synthesis of the gum.⁶ It is opined that if the gum acid did yield the phosphate ions in the solution, they would have been removed during the purification process. If not, its presence in traces could not account for acidity.

Electrometric measurements: (i) *Conductance:* The conductance of the solution was measured by a L. & N. Kohlrausch type slide wire bridge, with an audiofrequency oscillator, and a tuned audiofrequency amplifier. Two Jones and Bollinger cells⁷ and a flask cell, based on the design of Daggett, Bair and Kraus,⁸ were used. The cell constants were determined by the method of Jones and Bradshaw.⁹ All measurements were made in cells kept in a waterbath at $25 \pm 0.02^{\circ}\text{C}$. The conductance of the solvent was determined at the same time, and was subtracted to give the conductivity of the solution.

(ii) *Potentiometric measurements:* Hydrogen ion activity and total titratable acidity were determined by a Cambridge bench type potentiometer using a hydrogen electrode at $30 \pm 0.05^{\circ}\text{C}$. The platinum deposit of the electrode was removed and replatinized every day after measurements to avoid any error due to electrode contamination.

Viscosity measurements: Viscosity was determined using a modified Ostwald's type viscometer,¹⁰ having a smaller bulb contiguously below the efflux bulb with the time of flow of water equal to 100-150 seconds at 25°C . The viscometer was standardized for the uniformity of the capillary by determining the viscosity of the conductivity water and also of pure chloroform. The observed and the standard values for the viscosity of the above two liquids at the selected temperatures agreed fairly well. The viscometer was calibrated before use by a standard solution of cane sugar at 10% and 20% concentrations. Since the solutions were very dilute, the difference in the density of the solution and the solvent used was not very significant, and therefore, no density measurements were done for the determi-

nation of viscosity. Extra precautions were taken in keeping the viscometer very clean otherwise the values obtained were fairly high.

The viscometer with the solution was always kept in a fixed position, upright in a thermostat at a constant temperature. The viscosity was measured by observing the rate of efflux through the capillary. Time was noted within an accuracy of 0.1 second. The recorded time was the mean of the several timings. The mean of the time readings were used for calculating the viscosity. In each case the time of flow for the solution as well as for the water was measured. The relative viscosity was calculated by the formula $\eta/\eta_0 = tw/t_0 w_0$, where t and w denote the time of flow and the weight of the solution and t_0 and w_0 , the corresponding values for water. No kinetic corrections were made, because of the large time of flow, uniform capillary size, and the time taken by the solution and water did not differ considerably from each other.

Viscosity determinations were made for samples of sols, to which various amounts of non-electrolytes were added. The samples for the viscosity measurements were prepared in such a way that the colloid contents were always the same. Thus, any variation in the viscosity would be due to the changes in the character of the dispersed phase.

Analar chemicals were used.

RESULTS

Potentiometric titration of the gum acid with M/10 HCl, KOH, and Ba(OH)₂ is given in figure 1. The pH and conductance data of the gum acid with concen-

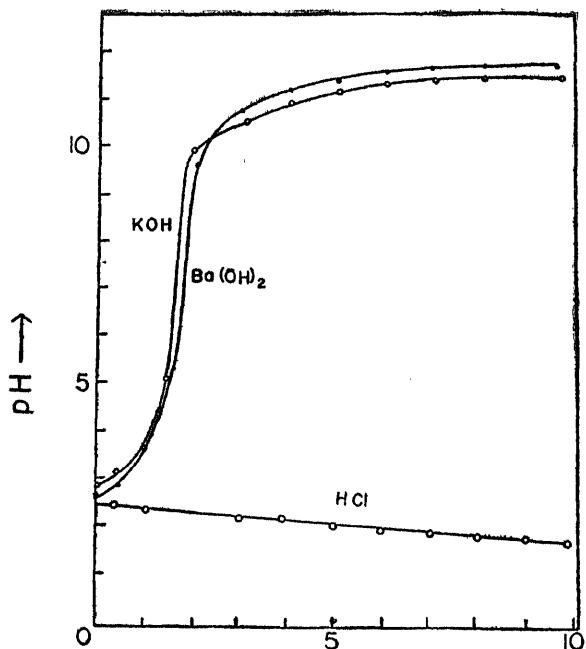


Fig. 1. Potentiometric Titration of the Gum Acid with 0.1 N HCl, KOH and Ba(OH)₂ respectively.

tration are recorded in the table 1. Table 2 shows the interaction of the gum with

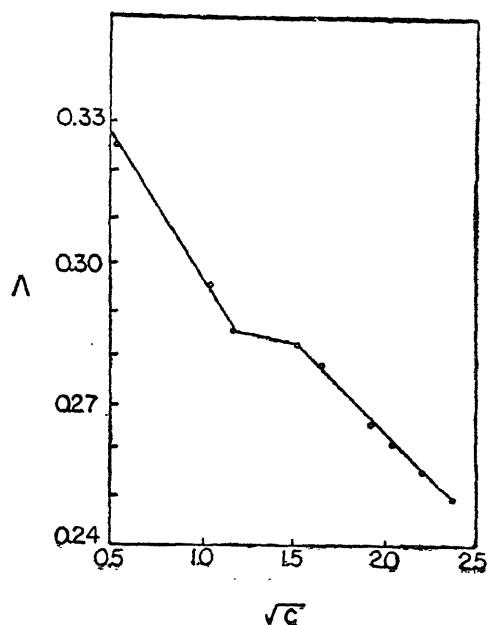


Fig. 2. Conductance versus square root of the concentration of the gum acid solutions.

TABLE I
pH and conductivity changes with the concentration of the Gum Acid

Conc. g./l.	C	pH	Sp. Cond. 10^3	Sp. Cond. 10^3 = Λ	
				Conc. g./l.	
7.5	2.738	1.64	1.824	24.87	
6.0	2.449	1.69	1.5556	25.93	
4.5	2.121	1.82	1.179	26.20	
3.6	1.899	1.93	1.119	26.60	
3.3	1.817	1.94	0.887	26.90	
3.0	1.732	1.97	0.823	27.46	
2.4	1.549	2.11	0.682	28.37	
1.8	1.341	2.20	0.531	28.54	
1.2	1.095	2.36	0.342	29.54	
0.3	0.545	3.13	0.977	32.59	

TABLE II
Interaction of the Gum with Non electrolytes

Conc. of Non-Electrolytes by vol. Percent	pH with						
	Methyl Ethyl Ketone	Ethyl Alcohol	Butyl Alcohol	Glucose	Cane Sugar	Urea	Acetone
10	3.58	3.54	3.64	3.94	3.67	5.84	3.72
20	3.62	3.63	3.62	3.59	3.51	6.76	3.64
30	3.67	3.66	3.50	3.57	3.39	7.99	3.70
40	3.73	3.74	3.44	3.56	3.30	7.55	3.69

some non-electrolytes. Figure 3 represents the variations in the relative viscosity of the gum with concentration. The changes in the relative viscosity as a function

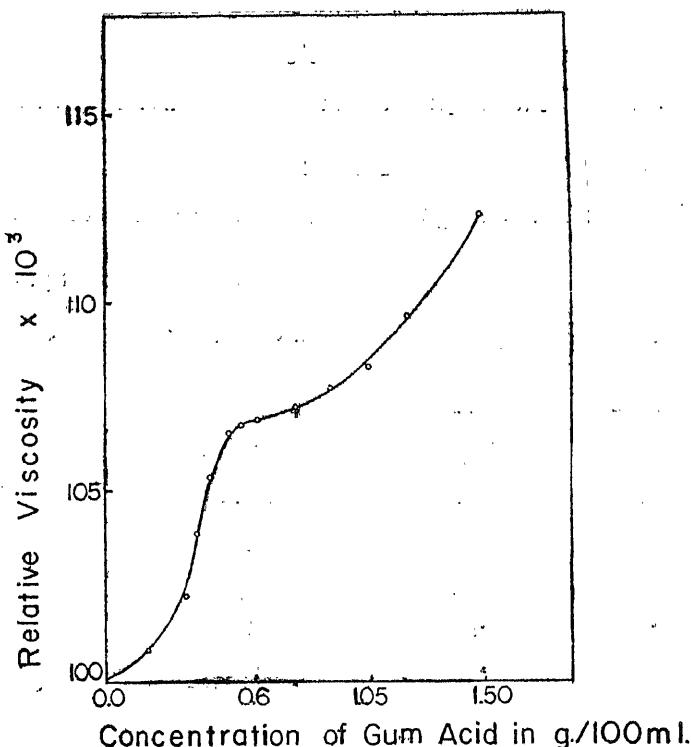


Fig. 3. Variations in the Relative Viscosity of the Gum Acid with concentration in g./100 ml.

of pH was determined, while keeping the concentration of the solute constant ($0.75\text{g}/100\text{ ml}$) and adding varying amounts of HCl and NaOH to obtain different pH. The relative viscosity changes with HCl are not reported here because it does not seem to be of interest due to a continuous decrease. However, the results with NaOH are given in figure 4. The results of the viscosity changes versus percentage

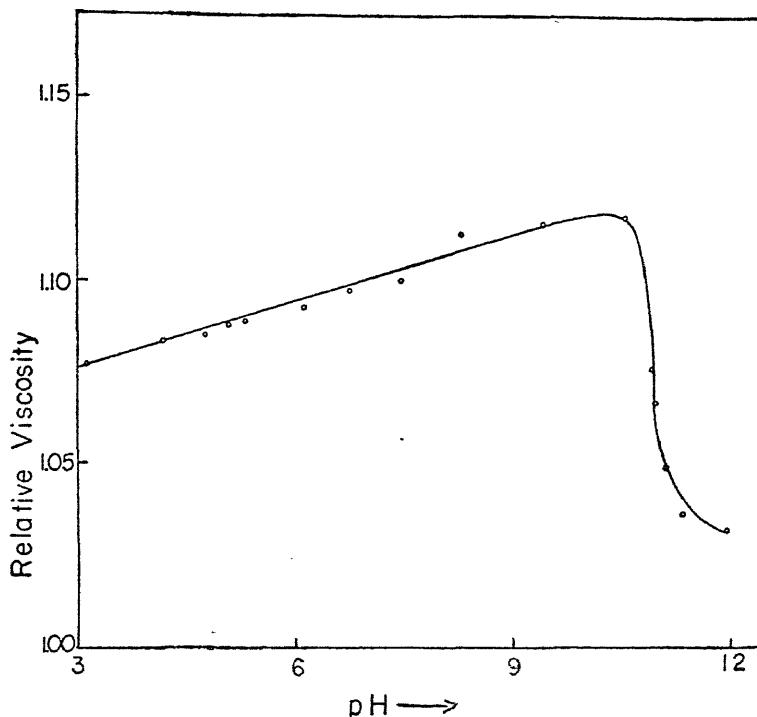


Fig. 4. Variations in the Relative Viscosity of the gum solution as a function of pH by the addition of NaOH.

of methyl alcohol added are given in the figure 5. In this experiment, the concentration of the gum acid solution was kept constant throughout for each set of observations, while methyl alcohol was added as another solvent in the increasing percentage by volume at $35 \pm 0.05^\circ\text{C}$.

DISCUSSION

The results for the electrometric titrations of the gum with 0.1 N HCl, KOH, $\text{Ba}(\text{OH})_2$, solutions are given in the figure 1. The neutralization curves for KOH and $\text{Ba}(\text{OH})_2$ are identical. Therefore it can be shown that the combination with alkali takes place in equivalent proportion. The curve for HCl indicates that the gum acid is not amphoteric in nature. All these conclusions are in closer agreement with the findings of Thomas and Murray with the gum arabic.¹¹

The graphical representation of Λ against \sqrt{C} has been given in the figure 2. Here Λ refers to the conductance offered by that volume of the solution containing one gram of the acid, because the equivalent weight of the acid is not known with certainty. A straight line curve is expected from the Onsager equation. The

figure shows the following features. Λ decreases linearly with \sqrt{C} at lower concentrations, but at higher concentrations, two kinks are also observed. According to McBain and Hartley¹² the kink indicates micelle or aggregate formation. Thus the gum acid shows the existence of aggregate formation. The other important feature of this curve is that Λ does not appear to pass through a minimum.

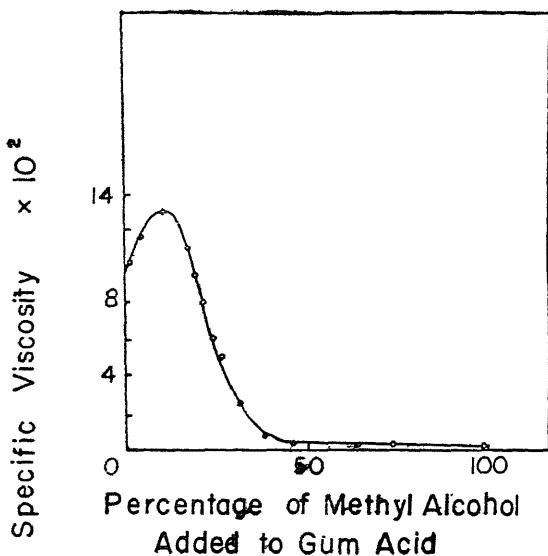


Fig. 5. Variations in the Specific Viscosity of the Gum Solution by the addition of varying percentage of Methyl Alcohol.

The interaction of the gum acid with non-electrolytes is recorded in table 2. The pH of the gum solution shows a simultaneous increase with the increasing concentration of methyl and ethyl alcohol. But in the case of butyl alcohol the pH values decrease. Methyl alcohol and methyl ethyl ketone have exactly identical influence on the pH changes. Cane sugar, glucose and acetone decrease the pH of the gum solution. These observations are not in agreement with those observed in the case of gum karaya and gum joel.¹³

Figure 3 represents the variation in the relative viscosity of the gum acid with concentration. It is a non-linear curve and a sudden increase in the slope is observed at a concentration of 0.5 g./100 ml. The increase in the viscosity is more rapid at higher concentrations. This kind of variation at higher concentrations has been regarded as a characteristic feature of lyophilic colloids.^{14,15} With increasing concentrations, water available for hydration of each miscelles is for less than in a dilute solution, where the degree of hydration is much greater. Molecules, associated with smaller number of water molecules bound to them at higher concentration, will necessarily have smaller dimensions and will tend to decrease the

viscosity. The net effect is determined by the simultaneously influencing factors such as aggregate-formation and hydration of the miscelles.

Figure 4 shows that on the addition of sodium hydroxide, the viscosity ratio increases slowly and linearly upto pH 7.5. Then it suddenly shoots up with a kink and attains a maximum value at pH 10.6. Beyond this point a very rapid fall in the relative viscosity is observed which becomes slow and steady beyond pH 11.5.

It is well known that the viscosity of solution is a function of the volume of the solute in the solution.¹⁶ The increase and decrease in the viscosity of the gum solution depends upon some mechanism, whereby the molecules increase and decrease their volumes. The changes in the viscosity with hydrogen concentration is in direct accord with results obtained by Thomas and Murray¹¹, Kruyt and Tendeloo,¹⁴ and Taft and Malm.¹⁵ According to these workers, the increase of the relative viscosity at higher concentrations is a characteristic feature of a lyophilic colloid.

It is evident from the above observation that the viscosity of the gum solution is sensitive to pH changes. A similar observation has been reported with the solution of Konjak Glucomannan.¹³ The viscosity of the solution first increases and then decreases in the presence of high concentration of alkali. On the addition of sodium hydroxide to the gum solution, the acid is converted into a sodium salt, which dissociates more and more. The effective charge on the polyion increases and the viscosity also increases. The viscosity is maximum near the neutralization point. The viscosity of the gum arabic is reported maximum near the neutral pH, and has been ascribed to the changes in the shape and size of the molecules.¹⁷ A solution of gum Tragacanth, whose molecules are elongated and possess a certain degree of linear character, show a maximum viscosity in the aqueous solution at pH 8.¹² Therefore, it seems quite clear that the maximum viscosity is attained at a point, where the polymer chain is stretched to its maximum value. The fall in the viscosity on further addition of sodium hydroxide can be explained by the folding chain theory, in conjunction with the mass action or common ion effect. Increase in the free ionic concentration due to the addition of sodium hydroxide to the polyelectrolyte solution enhances the association of the oppositely charged ions to the polyions by the mass action effect. This reduces the intermolecular coulombic repulsion, which causes the molecules to curl up, and hence the viscosity decreases. On the addition of a considerable amount of sodium hydroxide to the solution of the sodium salt, the coiling of the polyelectrolyte molecule increases, resulting in the further increase in the viscosity. The changes in the viscosity beyond at 11.5 can safely be ascribed to the denaturation of the proteins, which form a complex with carbohydrate polymer.

Figure 5, shows that the relative viscosity rises rapidly at lower percentage of the added solvent. It decreases with the increase of the volume percentage of the solvent, and after the addition of a certain amount of the solvent, it decreases very slightly.

Kruyt, Bundenberg de Jong and others have based their stability theory on the changes that the η_{sp} . of hydrophilic colloids show at constant colloid concentration, when the composition of the dispersion medium is systematically altered. Thus the results obtained show changes in the solvation. The rise in the η_{sp} . indicates some increase in the hydrodynamic volume unit. This type of behaviour is a characteristic of polyelectrolytes and distinguishes them from the other neutral polymers. The electroviscous effect takes into account only the presence of the electric charges on the rigid particle and its ion atmosphere in the solution. The resulting increase in the rate of the dissipation of energy and potential cause an increase in the viscosity. The molecules are large, highly polymerized and contain large number of COOH groups. The COOH groups ionize as COO^- and H^+ . When the solutions of these acids are diluted, the ionizable groups increase, the chain becomes more charged and this results in the rapid increase in the viscosity.

As the percentage of the solvent increases, the amount of water is minimised, and some of the oppositely charged ions are drawn back on the polymer chain due to the high charge density on the polyions. Thus, some of the charged centers of the polyions are neutralized. This results in the decrease of the viscosity. The polyelectrolyte chain is less stretched at the higher concentrations and consequently shows a greater fall at the higher percentage of solvent. It is observed that coiling up of the chains has the same result at constant polyelectrolyte concentration.^{3,14,18}.

The viscosity behaviour of polyelectrolytes has been very satisfactorily explained by the folding chain theory proposed by Fuoss and Strass,¹⁹ Fuoss,²⁰ Hermans and Overbeek,²¹ Katchalsky, Kunzle, and Kuhn.²² They assume that the increase of the η_{sp} . upon dilution is due to the expansion of the coiled polyions.

One of the authors (V. K. S.) is thankful to the Ministry of Education, Government of India, for the award of a fellowship during the tenure of this work.

REFERENCES

1. H. S. Oakley, *Trans. Farad. Soc.*, 32, 1360 (1936).
2. S. Basu, P. G. Dasgupta and A. K. Sircar, *J. Colloid Sci.* 6, (1951), 539; *ibid.* 9, 575 (1954).
J. van der Vies, *J. Phys. Chem.*, 57, 189 (1953).
3. R. M. Fuoss and G. I. Gathers, *J. Polymer Sci.*, 2, 12 (1947).

4. S. Mukerji and H. C. Srivastava, *Current Sci.*, India, **20**, 127 (1951).
5. A. P. Mathews, "Physiological Chemistry" Chapt. 11 (1926).
6. Beaquesne, *Compt. Rend.*, **222**, 1056 (1946).
7. G. Jones and G. M. Bollinger, *J. Am. Chem. Soc.*, **53**, 1780 (1933).
8. H. M. Daggett, E. J. Bair, and G. A. Kraus, *J. Am. Chem. Soc.*, **73**, 799 (1951).
9. G. Jones and B. C. Bradshaw, *J. Am. Chem. Soc.*, **55**, 1780 (1933).
10. R. K. Cannan, *Ind. Eng. Chem.*, **16**, 708 (1944).
11. A. W. Thomas and H. A. Murray, *J. Phys. Chem.*, **32**, 676 (1928).
12. J. W. McBain and A. Betz, *J. Am. Chem. Soc.*, **57**, 1909 (1935).
13. S. N. Mukherji and R. N. Raichawdhari, *J. Ind. Chem. Soc.*, **30**, 198 (1935).
S. N. Mukherji, *ibid.*, **30**, 201 (1953).
S. N. Mukherji, and S. N. Sinha, *ibid.*, **30**, 647 (1953).
14. H. R. Kruyt and H. J. C. Tendello, *Colloid. Chem. Beihft.*, **29**, 396 (1929).
15. R. Taft and L. Malm, *J. Phys. Chem.*, **35**, 874 (1934).
16. J. Loeb, "Protein Theory of Colloidal Behaviour," 1922.
17. W. Pauli and E. Ripper, *Kolloid-Z.*, **62**, 162 (1933).
W. Pauli and L. Palmrich, *Kolloid-Z.*, **79**, 63 (1937).
R. Taft, L. Malm, and D. R. Briggs, *J. Phys. Chem.*, **38**, 867 (1934).
18. H. R. Kruyt and H. G. Bundenberg de Jong, *Kolloid-Beih.*, **26**, 1 (1928).
H. G. Bundenberg de Jong, and O. S. Gwan, *ibid.*, **31**, 89 (1930).
H. R. Kruyt K. C. Winkler, *Kolloid. Chem., Beih.*, **32**, 374 (1931).
H. G. Bundenberg de Jong, H. R. Kruyt, And H. Lier, *Kolloid-Buh.* **36**, 429 (1932).
19. R. M. Fuoss, and U. P. Strass, *J. Polymer Sci.*, **3**, 246, 602 (1948).
20. R. M. Fuoss, *J. Polymer Sci.*, **3**, 603 (1948).
21. J. J. Hermans and J. Th. G. Overbeek, *Bull. Soc. Chim. Belges*, **57**, 421 (1948).
22. A. Katchalsky, O. Kunzle and W. Kuhn, *Helv. Chim. Acta*, **31**, 1948.

1. PEDOCHEMICAL CHARACTERISTICS OF SOME SOILS OF KOTA AND UDAIPUR DISTRICTS OF RAJASTHAN

By

S. SINGH and G. S. BHANDARI

College of Agriculture, Banares Hindu University, Varanasi-5

[Received on 9th July, 1962]

ABSTRACT

The results throw light on the morphological and pedochemical characteristics of three typical soil profiles of plateau and hilly tracts of Rajasthan. The soils show marked variation in mechanical composition suggesting differences in the degree of weathering undergone by the soil complex. All the soils invariably abound in plant mineral nutrients and contain fair amounts of carbon and nitrogen. The profile differentiations into well marked horizons are absent apparently because of their immature nature. Clays have been investigated in respect of their elementary composition and exchange capacity to have some idea of their nature, and also their possible significance in the formation of these soils.

It is suggested that soils of Kota region are old alluvium and those of Udaipur region *situ* formations. Indistinct horizons in the latter soils, however, suggest that they are in the process of formation.

Apart from the recent works of Singh and Bhandari (1 to 7) relating to the various organic matter fractions of Rajasthan soils, and a few scattered studies of Tamhane *et al*⁸, Tamhane and Rao⁹, Gupta¹⁰, and Mehta *et al*¹¹, very little appears to have been published on soils of the State and no systematic morphological and pedochemical studies appear to have been carried out. In view of this, the investigation reported in this paper was undertaken to provide some such information on three typical profiles sampled from plateau (Kota) and hilly tracts (Udaipur) of the State.

General features

Rajasthan lies between 23° 3' and 30° 12' N latitudes and 69° 30' and 78° 17' E. longitudes and commands a total geographical area of 132147·3 sq. miles. It stretches 510 miles from north to south and 540 miles from east to west. It is diverse land of immense desert tracts, plateaus, plains, hills and forestclad hilly area. Soils vary a great deal from area to area and the rainfall coupled with temperature predominantly governs the variegated growth of vegetation and cultivation of land throughout the State.

Climate

The plateau and hilly tracts constituting the south-east region of the State enjoy a fairly regular rainfall, mostly falling in June, July and August, and are never subjected to the extreme drought of western Rajasthan. Mean temperature and annual rainfall of the localities are given in Table 1

TABLE 1
Mean temperature and annual rainfall*

Locality	Annual rainfall in inch	Temperature in °F.			
		1958		1959	
		Max.	Min.	Max.	Min.
Kota	29.54	116.6	46.4	114.8	44.0
Udaipur	24.51	111.2	39.2	109.4	35.6

Geology

The plateau and hilly tracts of the south-east Rajasthan constitute mostly quartzite ridges which are considered to belong to the Alwar group of Delhi system. With them are associated bands of conglomerate containing boulders and pebbles of quartzite and a large area of granite gneiss, Schists, sandstones and limestones are also of common occurrence.

SOIL ANALYSIS

The soil samples were passed through 2 mm. sieve and used for analysis. HCl-extract was prepared by Hall's method and analysed as detailed by Piper¹¹. Calcium carbonate was determined by Hutchinson and MacLennan's¹² pipette method. Organic carbon was determined by rapid titration method of Walkley and Black¹⁴ and nitrogen by the Kjeldahl method as modified by Bal.¹⁵

The determination of total exchange capacity was made by the ammonium acetate method as described by Piper. pH was determined using glass electrode (1:2.5, Soil/Water ratio). The separation of clay fraction was done by Robinson's method as given by Wright,¹⁶ but the soil was boiled with water for 10 minutes instead of treating it with H_2O_2 to affect the breaking of soil aggregates. The clay was analysed after fusion with Na_2CO_3 .

*Source : A basic statistics of Rajasthan (1960) Govt. of Rajasthan Pub. Jaipur.

Site and Morphological Characters

TABLE 2
Morphological Description

Profile No.	Depth in inch	Description	Remarks
1	0-8	Very dark grey (D 10 YR3/1) clay loam, crumb structure, sticky and plastic when wet and hard when dry, deep vertical cracking when dry, effervescence, iron nodules, rootlets, freasy and neutral.	Slightly calcareous sub-stratum of 'Kankar' nodules in the bottom of the profile.
	8-32	Dark grey (D 10 YR 4/1) clay loam, blocky, sticky and tenaceous when wet, effervescence and neutral.	
	32-45	Light grey (D 10 YR7/1) clay loam, blocky, effervescence, sticky when wet, neutral.	
	45-55	Light grey (D 10 YR7/1) clay loam, blocky, profuse calcareous concretions, sticky when wet and slightly alkaline.	
	55-72	Light grey (D 10 YR7/1) clay loam, highly calcareous, under-developed and slightly alkaline.	
2	0-12	Dark reddish brown (D 2.5YR2/4) clay loam, non-sticky and friable when wet, iron nodules and neutral.	Distinct rock material mostly quartz and sandstones lie at the bottom of the profile.
	12-24	Reddish brown (D 2.5YR4/4) clay loam, non-sticky and friable when wet, gritty, small pieces of quartzstone, structureless and natural.	
	24-36	Reddish brown (D 2.5YR5/4) clay loam, pieces of quartzstones and iron nodules in abundance, structureless and neutral.	
	36-60	Reddish brown (D 2.5YR5/4) clay loam, abundance of quartzstones and iron nodules, structureless and natural.	
3	0-19	Vary dark grey (D 10 YR 3/1) sandy loam, granular non-sticky and friable when wet effervescence, profuse roots and neutral.	Highly calcareous sub-stratum consisting of 'Kankar' nodules of varying size and consistency at the bottom.
	9-20	Dark grey (D10 YR4/1) sandy loam, hollow tubes and calcareous concretions, friable and non-sticky when wet, granular, effervescence and neutral.	
	20-39	Light grey (D 10 YR7/1) sandy loam, profuse calcareous concretions, friable when wet, single-grained structure and slightly alkaline.	
	39-72	Light yellow (D 10 YR7/6) sandy loam, structureless, calcareous, under-developed and slightly alkaline.	

Profile 1 (Type 1) was sampled from Borkheda Govt. Farm Ladpur in Kota. The land is irrigated and topography is level. Water table is 20-30 feet. Genetically, the soils are old alluvium but the profile is not differentiated into distinct horizons. Wheat, barley, maize, jawar and cotton constitute main crops of the area.

The site for profile 2 (Type 2) was a cultivated land of Kadua village Farm adjoining Udaipur jaisamand road and at a distance of about 8 miles from Udaipur. The land is surrounded by hills and topography is not level but gently sloping southwards. Land is well irrigated and water-table is 30-40 feet. No distinct horizons are formed except the uppermost 1 foot layer which is somewhat darker in colour. Common crops grown are wheat, barley, maize and pulses.

Profile 3 (Type 3) was sampled from Koran village Farm beyond the outskirts of Kelva-Ki-nal', adjoining the same road and lies at a distance of 12 miles from Udaipur. Topographically, it is gently sloping southwards. The land is thickly surrounded by hills which are densely forest-clad. The soils are dark grey in colour and assume deeper colour when moist. These are highly fertile and wheat, barley, pulses and maize constitute the cropping vegetation. Water table is 20-30 feet.

There was absence of well marked horizons in all three profiles, although there were slight demarcations and therefore samples were taken according to them.

RESULTS AND DISCUSSION

Soil type one is very dark grey clay loam (Table 2). Almost all the morphological and physical properties of these soils are evidently manifestations of high content of clay, which is probably of montmorillonitic nature. These soils resemble somewhat to black soils of Bundel Khand region of U. P., studied by Agarwal *et al*¹⁷.

Soils 2 and 3 markedly vary in morphological features from the soil described above because they are *situ* formations of quite different parentage. More information to elucidate these statements is reported in the third paper of this series.

TABLE 3
Mechanical composition of soils
(Per cent on oven-dry basis)

Profile No.	Depth in inch	Mois-ture	Loss on ignition	CaCO ₃	Constituents			
					Coarse sand	Fine sand	Silt	Clay
1	0-8	6.1	6.07	2.19	0.34	31.35	14.00	52.25
	8-32	6.3	6.65	2.97	0.89	32.12	11.25	51.75
	32-45	6.0	6.71	3.92	0.58	33.22	12.25	45.25
	45-55	6.4	6.94	5.50	0.32	30.77	11.75	45.00
	55-72	3.1	10.90	16.00	1.20	38.05	11.75	32.00
2	0-12	3.7	5.37	—	8.61	33.65	22.25	34.75
	12-24	5.2	5.21	—	8.47	35.45	21.00	36.00
	24-36	5.3	5.58	—	7.22	32.49	19.50	39.45
	36-60	6.0	6.04	—	9.55	33.82	17.37	38.25
3	0-9	2.0	8.73	4.00	2.26	55.11	13.12	19.13
	9-20	2.4	6.63	5.50	6.67	52.01	15.10	19.22
	20-39	2.8	8.54	12.00	9.62	47.55	18.88	17.31
	39-72	1.9	12.51	19.50	13.82	42.73	16.35	16.07

Type 1. Loss on ignition figures increase with depth evidently as a result of increase in CaCO₃. Moisture figures decrease with depth presumably due to decrease in clay. The fine sand and clay fractions are high and together amount to 83.6 per cent in the surface layer. Clay decreases with depth while a reverse trend is shown by fine sand. The high contents of clay and fine sand signify greater decomposition in the surface.

Type 2. Moisture figures increase with depth and so is the case with loss on ignition with exception of the sample between 12 to 24 inches. The increase is evidently due to increase in clay. CaCO₃ is absent throughout the profile. The fine sand and clay fractions together amount to 68.40 and 72.02 per cent in the surface and bottom layers respectively, while silt gradually decreases with depth.

Type 3. Loss on ignition figures increase with depth evidently as a result of increase in CaCO₃. Silt and clay together amount to 32.25 and 32.42 per cents in surface and bottom layers respectively. The fine and coarse sand fractions together constitute almost 55 per cent of the soil separates signifying greater disintegration of the soil complex.

TABLE 4
Physicochemical Analyses
(Per cent on oven-dry basis)

Profile No.	Depth in inch	pH	Water holding capacity	T. B. E. C.*	Organic carbon	Total nitrogen	C/N	Total water soluble salts
1	0-8	7.8	52.4	45.5	0.372	0.079	4.7	0.18
	8-32	7.8	48.6	45.0	0.301	0.054	5.5	0.17
	32-45	7.9	49.1	43.0	0.300	0.053	5.6	0.14
	45-55	8.1	49.4	38.1	0.240	0.050	4.8	0.12
	55-72	8.1	48.3	30.3	0.205	0.035	5.8	0.08
2	0-12	6.9	42.8	27.7	0.574	0.097	5.9	0.05
	12-24	7.0	46.0	31.5	0.476	0.063	7.5	0.09
	24-36	7.0	46.0	32.2	0.420	0.067	6.2	0.08
	36-60	6.9	30.8	31.9	0.399	0.057	7.0	0.10
3	0-9	7.9	46.8	15.0	1.112	0.110	10.1	0.13
	9-20	7.8	44.2	14.9	0.723	0.078	9.2	0.12
	20-39	8.1	43.5	13.4	0.513	0.050	10.3	0.14
	39-72	8.2	45.2	10.1	0.367	0.033	11.1	0.14

Type 1. The pH is on alkaline side because of the presence of CaCO_3 . Water holding capacity decreases slightly with depth although not proportionally with clay. Therefore, it appears to be correlated with both clay and silt contents as the later in association with CaCO_3 under water-logged conditions is known to acquire feeble colloidal properties. The exchange capacity decreases with depth and seems to be correlated with the clay content. Organic carbon and nitrogen are high at the surface and decrease with depth. C/N ratios of soils of different layers range between 4.7 and 5.8. These figures suggest that the organic matter of these soils has been subjected to greater oxidative decomposition leading to comparatively more accumulation of nitrogen rich organic matter in the soil. This is in confirmation of the earlier findings of the authors that the high accumulation of N rich organic matter in these soils is presumably due to its association with the characteristic clay-humus complexes, resulting in stabilization in the tropical soils. Soluble salts are low but tend to accumulate at the surface evidently as a result of restricted drainage.

Type 2. The pH shows that the soil is almost neutral. Curious enough are the figures for water holding capacity. The exchange capacity follows the same trend as clay. Carbon and nitrogen show the same trend as in the soil 1, possibly

*Total base exchange capacity.

owing to the reasons discussed. Water soluble salts are low because of good drainage and low water-table.

Type 3. The pH is on the alkaline side and increases with depth owing to greater accumulation of CaCO_3 . Water holding capacity is nearly two and half times of the clay content, possibly due to high organic matter and feeble colloidal character of silt. The exchange capacity decreases with the depth evidently as a result of decrease in clay and organic matter. C/N ratios are wide as compared to those of the above two types, indicating less oxidative decomposition of organic matter in this soil type. Water soluble salts slightly higher than type 2 possibly due to high water table.

TABLE 5
HCl- Extract Analyses
(Per cent on oven-dry basis)

Profile No.	Depth in inch	HCl solubles	R_2O_3	Al_2O_3	Fe_2O_3	TiO_2	P_2O_5	CaO	MgO	K_2O
1.	0-8	31.42	21.11	11.60	8.68	0.71	0.120	1.32	0.99	1.92
	8-32	31.68	19.43	9.96	8.96	0.42	0.095	1.47	0.94	2.24
	32-45	31.83	19.90	10.05	8.85	0.89	0.110	1.88	1.03	1.44
	45-55	34.00	14.63	6.77	7.54	0.21	0.110	3.90	2.05	2.21
	55-72	39.20	16.57	9.06	7.26	0.13	0.120	8.49	1.20	1.44
2	0-12	25.63	16.90	8.56	8.14	0.12	0.038	0.68	0.93	0.48
	12-24	28.47	18.81	9.87	8.86	0.02	0.023	0.71	0.74	0.57
	24-36	30.15	20.12	10.44	8.34	0.29	0.019	0.67	0.75	0.64
	36-60	30.82	19.97	10.80	8.10	Trace	0.024	0.21	0.17	0.61
3	0-9	22.66	11.58	2.57	8.48	0.37	0.078	3.11	1.43	0.90
	9-20	35.06	11.56	3.60	7.37	0.47	0.049	3.61	1.15	0.90
	20-39	30.49	12.45	4.05	8.03	0.29	0.039	6.13	1.40	0.80
	39-72	36.72	12.97	3.59	8.73	0.57	0.032	10.09	1.40	0.61

Type 1. HCl-solubles increase with depth evidently as a result of higher accumulation of CaCO_3 . The sesquioxides amount to 21.11 per cent in the surface soil and decrease with depth possibly because of decrease in clay. The mineral constituents do not vary much throughout the profile. Phosphoric acid is almost uniformly distributed in all the depths. The oxides of calcium and magnesium show increased accumulation with depth.

Type 2. HCl solubles increase with depth, a trend similar to clay. An almost similar trend is shown by sesquioxides. The mineral composition varies a little in all the depths.

Type 3. HCl-solubles increase with depth evidently as a result of increase in CaCO_3 . The content of sesquioxides tends to vary little as that of clay. Alumina shows relative accumulation in the sub-soil while iron remains almost constant in all the layers. Phosphoric acid is high at the surface and decreases with depth while potash is almost evenly distributed throughout the profile,

TABLE 6
Clay Analyses
(Per cent on ignited basis)

Profile No.	Depth in inch	Molecular Ratios								
		SiO ₂	R ₂ O ₃	Al ₂ O ₃	Fe ₂ O ₃	TiO ₂	MgO	CaO	K ₂ O	T.B.E.C.* SiO ₂ /R ₂ O ₃ SiO ₂ /Al ₂ O ₃ SiO ₂ /Fe ₂ O ₃
355	1 0-8	51.69	36.48	19.29	16.27	0.92	5.79	1.90	2.39	99
	8-32	50.96	35.88	19.09	15.47	1.31	6.12	1.92	4.40	95
	32-45	48.02	37.71	18.17	18.93	0.61	8.17	2.79	2.71	90
	45-55	51.73	35.06	20.57	13.89	0.60	4.19	4.14	3.11	99
2	55-72	48.11	38.00	17.93	19.49	0.58	5.44	5.02	2.90	89
	0-12	47.44	44.31	23.19	20.76	0.36	0.39	0.31	4.20	49
	12-24	47.33	44.12	20.21	23.79	0.12	0.31	0.23	6.10	51
	24-36	48.31	44.29	24.14	20.14	0.01	0.27	0.92	2.72	51
	36-60	47.50	46.00	24.59	21.20	0.21	0.15	0.17	2.79	48
3	0-9	49.84	37.21	9.29	26.62	1.30	7.10	1.00	2.20	95
	9-20	51.86	36.00	11.81	23.38	0.81	6.83	1.21	3.01	100
	20-39	49.41	37.90	10.53	27.03	0.34	3.92	3.29	1.82	99
	39-72	48.91	39.56	13.67	25.28	0.61	4.39	5.12	2.00	93

*Total base exchange capacity

Type 1. Silica constitutes almost 50 per cent of the clay. Except in the fourth layer, where accumulation of silica is highest, it decreases with depth. Sesquioxides show uneven distribution tending to accumulate in the bottommost layer. Alumina tends to accumulate in the fourth layer. Iron oxide shows a trend similar to sesquioxides. It appears the weathering tends to deplete the soil more of its sesquioxides than silica. Magnesia increases with depth reaching maximum in the third layer and is low in the bottom layers. The $\text{SiO}_2/\text{R}_2\text{O}_3$ ratio shows little variation, the range being from 2.69-3.04. The $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio varies little, it being 4.29-4.58. The exchange capacity follows the same trend as silica. The results confirm immature nature of the profile and also indicate montmorillonitic nature of the clay.

Type 2. Silica figures vary little throughout the profile. Except in the bottom layer where sesquioxides are accumulated the highest, they are constant throughout the profile. Iron tends to accumulate in the second layer while it varies little in other layers. Magnesia and potash are high at the surface and decrease with depth. Calcium is low in the clays of all layers. The more or less constant composition of the clays of this type is possibly due to its not being subjected to the leaching process. The $\text{SiO}_2/\text{R}_2\text{O}_3$ and $\text{SiO}_2/\text{Fe}_2\text{O}_3$ ratios are almost constant in all the depths. The exchange capacity follows the trend of silica. These facts appear to confirm relatively more immature nature of the profile and the clays of the mixed mineral build.

Type 3. Silica is high in the second layer and tends to remain somewhat constant in other layers. With exception of the second layer, sesquioxides increase with depth. The content of alumina shows a tendency of deposition in the sub-soil. Iron oxide is high in the surface layer. The calcium content increases with depth. It appears that weathering has enriched the sub-soil more of its iron and alumina than silica. This evidence confirms the immature nature of the profile, although the soil complex appears to have been subjected to greater weathering than the previous type. The $\text{SiO}_2/\text{R}_2\text{O}_3$ ratios vary a little, they being 2.8-3.3. $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios vary from 6.08-9.23. The $\text{SiO}_2/\text{Fe}_2\text{O}_3$ ratio is somewhat constant. The exchange capacity ranges between 93.5 and 100.0 milli-equivalents per 100 gm. These values may suggest the predominance of montmorillonitic or other high exchange clays in the soil type.

ACKNOWLEDGEMENTS

The authors wish to express their sincere thanks to the Ministry of Scientific Research and Cultural Affairs, Govt. of India for a research scholarship to the junior author.

REFÉRENCES

1. Singh, S. and Bhandari, G. S., *B. H. U., J. Scientific Res.*, **13**, 73 (1962).
2. Singh, S. and Bhandari, G. S., *Ibid*, **13**, 132 (1962).
3. Singh, S. and Bhandari, G. S., *Ibid*, **13**, 138 (1962).
4. Singh, S. and Bhandari, G. S., *J. Indian Soc. Soil Sci.*, **11**, 1 (1963).
5. Singh, S. and Bhandari, G. S., *B. H. U., J. Scientific Res.*, **13**, 240 (1963).
6. Singh, S. and Bhandari, G. S., *J. Indian Soc. Soil Sci.* **11**, 152 (1963).
7. Singh, S. and Bhandari, G. S., *J. Soil Sci.* (under publication), 1964.
8. Tamhane, R. V. et al, *Ibid*, **1**, 105, (1953).
9. Tamhane, R. V. et. al. and Rao, N., *Ibid* **4**, 105 (1956).
10. Gupta, R. S., *Ibid*, **6**, 115 (1958)
11. Mehta, K. M. et al., *Ibid* **6**, 125 (1958).
12. Piper, C. S., *Soil and Plant Analysis* (1950).
13. Hutchinson, H. B. and MacLennan, K., *J. Agric. Sci.*, **6**, 323 (1914).
14. Walkley, A. and Black, I. A., *Soil Sci.*, **37**, 29 (1934).
15. Bal, D. V., *J. Agric. Sci.*, **15**, 454, (1925).
16. Wright, C. H., *Soil Analysis* (1939).
17. Agarwal, R. R., et al, *J. Indian Soc. Soil Sci.*, **4**, 65, 1956.

INVESTIGATION OF 851 DOUBLES IN THE OXFORD ASTROGRAPHIC
CATALOGUES $+30^\circ$ AND $+31^\circ$ WITH ANGULAR SEPARATION
LESS THAN $15''$ (PART III)

By

A. N. GOYAL and S. S. MITHAL

Department of Mathematics, University of Rajasthan, Jaipur

[Received on 29th May, 1964]

ABSTRACT

The present paper is a continuation of two previous papers (1, 2) and gives the results of the search and counts of 851 doubles with an angular separation less than $15''$, in Oxford Astrographic Catalogues $+30^\circ$ and $+31^\circ$, in different magnitudes and for different values of Δm (the difference of magnitude between the components.). The ratio T: O (Observed to Optical) from Struve and Kreiken's formulae are given. The values of T: O are compared with the ones given in (1, 2). The agreement is fairly good. The average galactic concentration obtained by comparing the distributions in galactic latitudes $0^\circ < |\beta| \leqslant 20^\circ$ and $|\beta| > 40^\circ$ works out to be 5.38 which is smaller than the zones $+32^\circ$ and $+33^\circ$ (7.77), $+26^\circ$ and $+25^\circ$ (6.09). The average galactic concentration for all stars in these zones is found to lie between 2.24 and 3.07 . The average galactic concentration for doubles in these zones is larger than the average galactic concentration for stars themselves a conclusion reached in the zones $+32^\circ$, $+33^\circ$, $+26^\circ$ and $+25^\circ$ of the Oxford Astrographic Catalogues. The method of investigation remains the same as described in the paper referred to.

Observed distribution of stars according to d and Δm

TABLE 1

($+30^\circ$) $0'' < d \leqslant 5''$

$\frac{\Delta m}{m}$	0.0	·3	·6	·9	1.2	1.5	1.8	2.1	2.4	>	T	0
< 9.0	1	0	0	0	0	0	0	0	0	0	1	0.82
10.0	2	0	1	0	0	1	0	2	0	6	1.19	
11.0	6	5	2	2	5	1	1	0	0	22	0.90	
12.0	10	9	5	5	4	0	0	0	0	33	3.71	
13.0	6	1	1							8	3.00	
$>$	1									1	...	

TABLE II
 $(+30^\circ)$ $5'' < d \leq 10''$

$\frac{\Delta m}{m}$	0·0	·3	·6	·9	1·2	1·5	1·8	2·1	2·4	>	T	0
<9·0	0	1	0	1	0	2	1	2		4	11	7·38
10·0	2	4	0	3	5	2	1	3		5	25	10·71
11·0	5	8	3	5	7	4	5	0		1	38	8·10
12·0	19	13	7	4	1	0	0	0		0	44	33·39
13·0	16	13								29		27·00
>	1	3								4		...

TABLE III
 $(+30^\circ)$ $10'' < d \leq 15''$

<9·0	1	1	1	1	2	0	1	2	18	27	22·14
10·0	2	1	0	4	3	3	3	2	8	26	32·13
11·0	6	7	4	6	3	3	3	1	0	33	24·30
12·0	15	15	13	10	5	4	1	0	0	63	100·17
13·0	28	9	2						39		81·00
>	2	1	1						4		...

TABLE IV
 $(+31^\circ)$ $0'' < d \leq 5''$

<9·0	1	0	1	0	0	0	0	0	0	2	0·07
10·0	1	1	1	1	0	1	0	0	1	6	0·94
11·0	2	3	3	3	2	1	0	0	0	14	0·84
12·0	7	3	4	2	0	0	0	0	0	16	3·28
13·2	7	6	4						17		3·05
>	2								2		...

TABLE V
 $(+31^\circ) 5'' < d \leq 10''$

$\frac{\Delta m}{m}$	0·0	·3	·6	·9	1·2	1·5	1·8	2·1	2·4	>	T	0
$< 9·0$	0	0	0	2	1	0	0	0	0	4	7	0·63
10·0	2	2	3	3	0	2	1	4	4	21	8·46	
11·0	4	4	11	8	7	6	4	4	2	50	7·56	
12·0	26	16	14	10	3	1	0	0	0	70	29·52	
13·0	23	3	7	3	1					37	27·54	
>	3									3		

TABLE VI
 $(+31^\circ) 10'' < d \leq 15''$

$< 9·0$	0	0	0	1	1	2	2	0	19	257	1·89
10·0	2	1	2	0	1	6	6	4	4	26	25·38
11·0	4	3	4	5	8	5	6	4	3	42	22·68
12·0	20	21	10	5	1	3	0	1	0	61	88·56
13·0	22	7	4	2					35	82·35	
>	2								2		...
Total											
$+30^\circ 0'' < d \leq 5''$	26	15	9	7	9	2	1	2	0	71	9·62
$5'' < d \leq 10''$	43	42	10	13	13	8	7	5	10	151	86·58
$10'' < d \leq 15''$	54	34	21	21	13	10	8	5	26	192	259·74
$+31^\circ 0'' < d \leq 5''$	20	13	13	6	2	2	0	0	1	57	8·18
$5'' < d \leq 10''$	58	25	35	26	12	9	5	8	10	183	73·62
$10'' < d \leq 15''$	50	32	20	13	11	16	14	9	26	191	220·86

TABLE VII

Declination	doubles	0" - 5"	5" - 10"	10" - 15"
+30°	T	71	151	192
	O _s	5.271	47.439	142.232
	O _k	9.620	86.580	259.740
+31°	T	57	188	191
	O _s	5.119	46.071	138.213
	O _k	8.180	73.620	220.860
+30°	T : O _s	13.470	3.183	1.350
	T : O _k	7.380	1.744	0.739
+31°	T : O _k	11.135	4.081	1.382
	T : O _s	6.968	2.554	0.865
+25°	T : O _s	7.648	2.586	1.019
	T : O _k	7.231	2.444	0.963
+26°	T : O _s	8.816	2.835	1.014
	T : O _k	7.966	2.586	0.928
+32°	T : O _s	11.073	3.423	1.030
	T : O _k	9.760	2.933	0.930
+33°	T : O _s	9.177	2.750	0.894
	T : O _k	8.169	2.442	0.795

O_s and O_k are the number of opticals from Struve and Kreiken's formula.
Observed distribution of stars according to d , Δm and β .

TABLE VIII

(+30° and +31°); 0" < $d \leq 5"$; $0^\circ < |\beta| \leq 20^\circ$.

$\frac{\Delta m}{m}$	0.0	.3	.6	.9	1.2	1.5	1.8	2.1	2.4	>	T
<9.0	0	0	1	0	0	0	0	0	0	1	
	2	0	1	1	0	0	0	1	0	5	
10.0	7	2	2	3	5	1	1	0	0	21	
11.0	12	6	6	4	3					31	
12.0	7	5	4							16	
13.0		3									3
<											

TABLE IX

 $(+30^\circ \text{ and } +31^\circ); 0'' < d \leq 5''; 20^\circ < |\beta| \leq 40^\circ$

$\frac{\Delta m}{m}$	0·0	·3	·6	·9	1·2	1·5	1·8	2·1	>	T
>9·0	1	0	0	0	0	0	0	0	0	1
10·0	1	1	0	0	0	0	0	1	0	3
11·0	0	6	0	0	1	0	0	0	0	7
12·0	5	4	2	3						14
13·0										3

TABLE X

 $(+30^\circ \text{ and } +31^\circ); 0'' < d \leq 5''; |\beta| > 40^\circ$

<9·0	1	0	0	0	0	0	0	0	0	1
10·0	0	0	1	0	0	2	0	0	1	4
11·0	1	0	3	2	1	1	0	0	0	8
12·0	0	2	1	0	1	0	0	0	0	4
13·0	3	2	1							6

TABLE XI

 $(+30^\circ \text{ and } +31^\circ); 5'' < d \leq 10''; 0^\circ < |\beta| \leq 20^\circ$

<9·0	0	0	0	1	1	1	1	1	6	11
10·0	3	1	2	1	4	4	1	5	2	23
11·0	0	6	4	7	8	4	6	3	1	39
12·0	23	17	13	11	2	1				67
13·0	28	10	4	3	1					46
>	3	3								6

TABLE XII

 $(+30^\circ \text{ and } +31^\circ) 5'' < d \leq 10''; 20^\circ < |\beta| \leq 40^\circ$

$\frac{\Delta m}{m}$	0.0	.3	.6	.9	1.2	1.5	1.8	2.1	2.4	>	T
>9.0	0	1	0	2	0	1	0	0	2	6	
10.0	1	3	0	4	1	0	1	1	5	16	
11.0	9	3	6	2	3	4	2	2	1	32	
12.0	14	12	6	3	2					37	
13.0	8	5	1							14	
>1										1	

TABLE XIII
 $(+30^\circ \text{ and } +31^\circ); 5'' < d \leq 10''; |\beta| > 40^\circ$

<9.0	0	0	0	0	0	0	0	1	0	1	
10.0	0	2	1	1	0	0	0	1	2	7	
11.0	0	3	4	4	3	2	1	0	1	18	
12.0	8	2	2							12	
13.0	3	1								4	

TABLE XIV
 $(+30^\circ \text{ and } +31^\circ); 10'' < d \leq 15''; 0^\circ < |\beta| \leq 20^\circ$

<9.0	1	0	1	2	0	2	3	2	26	37	
10.0	2	1	1	0	1	9	7	1	9	31	
11.0	6	5	4	8	9	4	6	3	3	48	
12.0	24	27	16	9	6	5	1	1	0	89	
13.0	41	12	3	2						58	
$>$	4	1	1							6	

TABLE XV

 $(+30^\circ \text{ and } +31^\circ); 10'' < d \leq 15''; 20^\circ < |\beta| \leq 40^\circ$

$\frac{\Delta m}{m}$	0·0	·3	·6	·9	1·2	1·5	1·8	2·1	2·4	>	T
<9·0	0	1	0	0	2	0	0	0	0	10	13
10·0	2	1	0	4	2	0	1	3	1	14	
11·0	4	3	2	2	2	2	0	1	0	16	
12·0	8	6	3	6	0	1				24	
13·0	8	3	1							12	

TABLE XVI

 $(+30^\circ \text{ and } +31^\circ); 10'' < d \leq 15''; |\beta| > 40^\circ$

<9·0	0	0	0	0	1	0	0	0	1	2
10·0	0	0	1	0	1	0	1	2	2	7
11·0	0	2	2	1	0	2	3	1	0	11
12·0	3	3	4	0	0	1				11
13·0	1	1	2							4
$0'' < d \leq 5''$; $0^\circ < \beta \leq 20^\circ$	31	13	14	8	8	1	1	1	0	77
$20^\circ < \beta \leq 40^\circ$	10	11	2	3	1	0	0	1	0	28
$ \beta > 40^\circ$	5	4	6	2	2	3	0	0	1	23
$5'' < d \leq 10''$; $0^\circ < \beta \leq 20^\circ$	57	37	23	23	16	10	8	9	10	192
$20^\circ < \beta \leq 40^\circ$	33	24	13	11	6	5	3	3	8	106
$ \beta > 40^\circ$	11	8	7	5	3	2	1	2	3	42
$10'' < d \leq 15''$; $0^\circ < \beta \leq 20^\circ$	78	46	26	21	16	20	17	7	38	269
$20^\circ < \beta \leq 40^\circ$	22	14	6	12	6	3	1	4	11	79
$ \beta > 40^\circ$	4	6	9	1	2	3	4	3	3	35

REFERENCES

(42) Goyal A. N., M. N. R. A. S. 123, 413, 1962; M. N. R. A. S. 127, 341, 1964.

EMPIRICAL APPROACH FOR THE DETERMINATION OF WATER REQUIREMENTS OF CROPS

By

A. P. BHATTACHARYA

Research Officer, Basic Research Division, Irrigation Research Institute, Roorkee, U. P.

[Received on 25th October, 1962]

ABSTRACT

A solution to the problem of correct water requirements of crops is sure to lead to proper usage of water for irrigation and consequential rise in crop production. This is assuming greater importance at the moment because of shortage of food in the country and also because there is enough evidence of over-irrigation on the part of the cultivator wherever water is available for irrigation, which not only results in wastage of irrigation waters but also causes a drop in crop production. The problem can best be tackled by the experimental determination of water requirements of crops. But where no experimental data is readily available or feasible, recourse can be taken to the empirical approach by the use of a number of standard formulae including those of Lowry-Johnson, Thornthwaite, Blaney-Criddle, Penman, Hargreaves, Van Bavel. Blaney-Criddle formula gave the best analogy with observational data. The use of this formula is therefore recommended for the assessment of water for irrigation from climatological data.

1.0. INTRODUCTION

1.1. Apart from the experimental determination of water requirements of crops, which is dependent upon continuous experimentation for a number of years in order to smoothen the vagaries of weather variations from year to year, there are empirical methods which may be utilized for the determination of water requirements of crops from climatological data alone. Their utility lies in ready assessment for the framing of irrigation projects requiring an idea of the cropping pattern as also the watering needs of various crops proposed to be irrigated from climatological details alone when no experimental data are forthcoming. Besides, they also serve as a valuable check-up of the observational data.

1.2. This information regarding water requirements of various crops may then be utilized for computing the consumptive use or total water requirements for a valley or an entire project area.

2.0. EMPIRICAL FORMULAE

2.1. A few standard empirical formulae for the assessment of irrigation requirements from climatological data are described in the succeeding paragraphs. In this connection, it may be mentioned that experiments on water requirements of wheat were carried out at the Government Agriculture Farm, Dhanauri, for which detailed experimental and climatological data was available for the years 1956-57, 1957-58 and 1960-61. The latter was utilized for testing the applicability of the empirical formulae.

2.2. Among these formulae, one of the earliest was that advocated by R. L. Lowry and A. F. Johnson of the United States Bureau of Reclamation.¹ The Lowry-Johnson method is used to estimate valley consumptive use for agriculture with the aid of a linear relationship between "Effective heat" (the accumulation, in day degrees, of maximum daily growing season temperatures above 32°F) and consumptive use, namely, $U = 0.0015H + 0.9$, where U is the consumptive use,

H the accumulated degree days during the growing season. Consumptive use in a valley or drainage area involves water losses from non-agricultural parts of the area as well as agricultural lands. The Lowry-Johnson method requires the determination of an "equivalent valley area" of agricultural lands in order to arrive at the estimated annual consumptive use rate.

2.2.1. Tables 1(a) to 1(d) give the calculations for irrigation requirements at Dhanauri during the growing season of wheat, comprising the months of November to February. In Table 1(a), consumptive use has been deduced from Lowry-Johnson equation. Table 1(c) is based upon a curve assumed by Lowry-Johnson, wherefrom effective precipitation was worked out from actual precipitation, the former being taken as R in Table 1(d). Irrigation efficiency or water application efficiency is taken to be 70% in Table 1(d) of the basis of field trials conducted both in India and the United States of America wherefrom it is indicated that even in best prepared fields, 30% application losses bring down the irrigation efficiency to 70%. The calculations were done for three seasons, 1956-57, 1957-58 and 1960-61, during which the experiments on water requirements of wheat were conducted at Dhanauri. The mean irrigation requirement worked out to 22.83 inches, which is considerably higher than the experimental figure.

TABLE 1(a)
Effective Heat in Day-Degrees for Dhanauri, Uttar Pradesh, India during the growing season of wheat

Month	1956-57	1957-58	1960-61
November	1.383	1.366	1.482
December	1.262	1.116	1.359
January	1.073	1.144	1.195
February	1.135	1.159	1.052
Total	4.852	4.775	5.088
Consumptive use in feet	1.63	1.62	1.66

TABLE 1(b)
Showing monthly precipitation in inches at Dhanauri during the growing season of wheat

Month	1956-57	1957-58	1960-61
November	0.83	0.39	0
December	0	2.66	0.48
January	4.47	0.18	0.79
February	0.03	0.30	6.30
Total	5.33	3.53	9.57

TABLE 1 (c)

Effective precipitation from actual precipitation in inches

Actual	Effective
1	0·95
2	1·85
3	2·67
4	3·33
5	3·82
6	4·02
7 and over	4·10

TABLE 1(d)

Irrigation requirements at Dhanauri for the growing season of wheat by Lowry-Johnson method

Year	U in inches	R in inches	U - R in inches	I = $(U - R)/E$ in inches
1956-57	19·56	3·89	16·67	22·39
1957-58	19·44	3·00	16·44	23·49
1960-61	19·92	4·10	15·82	22·60
				Mean 22·83

2·3. The next approach was that of the formula advocated by H. F. Blaney and W. D. Criddle of the United States Department of Agriculture, which has been used successfully in many tropical countries.² In the Blaney-Criddle formula, consumptive use is found by multiplying together mean monthly temperature, monthly per cent of annual daytime hours and the crop coefficient, denoted by K. Figures for the latter were based upon a series of experiments, conducted in the Western United States, relating consumptive use to the climatic data. The sites of the experimental stations in Western U. S. have a strong resemblance in climatic characteristics with those of Dhanauri. The value of K for such areas was indicated to be 0·70 for grains with a growing season of 4 to 5 months.

2·3·1. By multiplying the mean monthly temperature, t , by the monthly percentage of daytime hours of the year, p , there is obtained a monthly consumptive use factor, f .

2·3·2. Expressed mathematically,

$$U = KF = \text{sum of monthly } Kf's,$$

where U = consumptive use of crop in inches during the growth season,

F = sum of the monthly consumptive use factors for the period (sum of the products of mean monthly temperature and monthly percent of annual daytime hours) $(t \times p)/100$,

K = empirical coefficient (annual or irrigation season or growing season),

t = mean monthly temperature in degrees Fahrenheit,

p = monthly percent of daytime hours of the year (from "Sunshine Tables", United States Weather Bureau, Bulletin 805),

f = monthly consumptive use factor,

$u = Kf$ = monthly consumptive use in inches.

2·3·3. On the basis of this formula, calculations are shown in Table 2 for the growing season of wheat at Dhanauri. Irrigation requirement at the head of the field is found to be 8·31 inches from this formula. From actual experimental results, it was found that two irrigation treatments of 3 inches each gave the maximum yield. If to this be added a pre-sowing irrigation of 2·5 inches, the total irrigation requirements work out to 8·50 inches, which agrees very closely with the theoretical figure of 8·31 inches arrived at from Blaney-Criddle formula. It may be added that this formula is being used successfully in many tropical countries and Europe besides the United States of America. The agreement with the experimental results from Dhanauri is very close.

2·4. Another approach used was the "Energy Balance Method". With this method, the assumption is made that the energy received by a surface through radiation must equal (i) the energy used for evaporation, (ii) heating the air, (iii) heating the soil, and (iv) any extraneous or advective energy. For short periods, such as daily and monthly balances, the latter two items may be neglected without seriously affecting the accuracy.

2·4·1. The application of this method requires the estimating or measuring of the energy received by a surface and deciding how this energy will divide itself between heating of the air and evaporation of the water. Distribution has been assumed to take place according to the so-called "Bowen ratio" fraction depending on temperature and vapour pressure at the surface and at some height above it.

2·4·2. In 1948, Dr. H. L. Penman, a physicist of Rothamsted Experimental Station, Rothamsted, U. K., suggested a method of estimating or measuring the amount of radiative energy gained by the surface which was expressed in mm. of water evaporated⁽³⁾. The method has been used widely in England, Australia and Eastern United States. Detailed calculations for the Penman formula are shown in Table 3(a), which gives the evapotranspiration losses or consumptive use for the growing season of wheat at Dhanauri.

2·4·3. The following three formulae are used by Penman in estimating evapotranspiration :

$$(i) H = R_A (1 - r) (0.18 + 0.55 n/N) - T_a^4 (0.56 - 0.092/r_d) \\ (0.10 + 0.90 n/N)$$

$$(ii) E_a = 0.35 (r_a - r_d) (1 + 0.0098 u_2) \text{ and}$$

$$(iii) F_T = (H + 0.27 E_a) / (\Delta + 0.27),$$

TABLE 2

Showing computations of irrigation requirements for the growing season of wheat at Dhanauri on the basis of
Blaney-Criddle formula

Month	Mean temperature (t) °F			Percent daytime			Monthly consumptive use factor (f)			Monthly rainfall (r) in inches			Remarks
	1956-57	1957-58	1960-61	hours (P)	1956-57	1957-58	1960-61	1956-57	1957-58	1960-61	1957-58	1960-61	
November	65·0	64·4	64·4	7·19	4·67	4·63	4·63	0·83	0·39	0	Percent daytime hours have been computed from Sunshine Tables, U. S. Weather Bureau Bulletin 6·30 805, 1905 edition, for a latitude of 30°N (for Dhanauri).		
December	58·2	57·9	59·1	7·14	4·23	4·13	4·23	0	2·66	0·48	Percent daytime hours have been computed from Sunshine Tables, U. S. Weather Bureau Bulletin 6·30 805, 1905 edition, for a latitude of 30°N (for Dhanauri).		
January	55·5	58·1	57·3	7·30	4·12	4·24	4·18	4·67	0·18	2·79			
February	57·6	59·4	56·7	7·03	4·05	4·18	3·96	0·03	0·30	6·30			
								17·07	17·18	17·01	5·33	5·53	9·57
								(F)	(R)				
Year	F	K	U = KF	R	U - R	Irrigation Efficiency, E	I = (U - R)/E						
1956-57	17·07	0·70	11·93	5·33	6·62	70%	9·46						
1957-58	17·18	0·70	12·03	3·53	8·50	70%	12·14						
1960-61	17·01	0·70	11·91	9·57	2·34	70%	3·34						
						Mean	8·31						

TABLE 3(a)

Showing details of calculations of evapotranspiration losses or consumptive use in inches for the growing season of wheat at Dhanauri by Penman method

	(c) $\sqrt{\epsilon_d}$...	3.39	3.14	2.60	3.02	3.18	3.01	2.54	2.80	2.67	3.04	2.70
11.	σ_{E_a}	...	14.57	13.82	13.60	13.71	14.46	13.75	13.90	14.45	13.80	13.69	13.31
12.	$(0.56 - 0.092/\epsilon_d)$...	0.25	0.28	0.27	0.32	0.29	0.27	0.28	0.33	0.30	0.31	0.28
13.	$(0.10 + 0.90n/N)$...	0.86	0.60	0.59	0.84	0.85	0.66	0.67	0.73	0.92	0.72	0.75
14.	Item 11 \times Item 12 \times Item 13	...	3.13	2.32	2.17	3.69	3.56	2.45	2.58	3.35	3.99	3.29	2.87
15.	Item 9 $-$ item 14 $= H$...	1.24	0.52	0.89	1.27	0.81	0.63	0.80	1.06	0.65	0.20	0.83
16.	$0.35 (\epsilon_a - \epsilon_d)$...	1.92	1.75	1.09	2.19	2.40	1.36	1.72	2.64	2.86	2.40	1.32
17.	$(1 + 0.0038U_3)$...	1.55	1.60	1.79	2.06	1.61	1.60	1.63	1.90	1.46	1.75	1.62
18.	Item 16 \times Item 17 $= E_a$...	2.98	2.80	1.95	4.51	3.86	2.18	2.80	5.02	4.18	4.20	2.14
19.	Δ	...	0.57	0.47	0.44	0.45	0.45	0.55	0.45	0.46	0.48	0.55	0.47
20.	ΔH	...	0.71	0.24	0.39	0.57	0.44	0.28	0.37	0.51	0.36	0.09	0.37
21.	$0.27 E_a$...	0.80	0.76	0.53	1.22	1.04	1.59	0.76	1.36	1.13	1.13	0.57
22.	$\Delta + 0.27$...	0.84	0.74	0.71	0.72	0.82	0.72	0.73	0.75	0.82	0.74	0.72
23.	$E_T = \frac{\Delta H + 0.27 E_a}{\Delta + 0.27} \text{ mm. of H}_2\text{O/day}$...	1.80	1.35	1.30	2.48	1.80	1.21	1.55	2.50	1.82	1.65	1.31
24.	Inches of H_2O/day	...	0.071	0.053	0.051	0.097	0.071	0.048	0.061	0.098	0.072	0.065	0.052
25.	Inches of $H_2O/\text{day month}$...	2.13	1.64	1.58	2.72	2.13	1.49	1.89	2.74	2.16	2.02	1.61

[371]

where H = Daily heat budget at surface in mm. H_2O/day ,
 R_A = Mean monthly extra terrestrial radiation in mm. H_2O/day ,
 r = Reflection coefficient of surface,
 n = Actual duration of bright sunshine,
 N = Maximum possible duration of bright sunshine,
 σ = Boltzman constant
 $= 2.01 \times 10^{-9}$ mm./day,
 $\sigma T_a^4 =$ mm. H_2O/day (see Table 3(a)),
 e_d = Saturation vapour pressure at mean dew point (*i.e.* actual vapour pressure in air) mm. H_g ,
 E_a = Evaporation in mm. H_2O/day ,
 e_a = Saturation vapour pressure at mean air temperature in mm. H_g ,
 u_2 = Mean wind speed at 2 meters above the ground (miles/day),
 E_T = Evapotranspiration in mm. H_2O/day ,
 u_1 = measured wind speed in miles per day at a height of h feet,
 Δ = Slope of saturated vapour pressure curve of air at absolute temperature T_a in °F. (mm. H_g F.).

2.4.4. Irrigation requirements are deduced in Table 3(b), in which consumptive use or evapotranspiration during the growing season is found from the Penman formula, explained above. Using a value of 70% for E , irrigation requirements, I , were worked out for wheat at Dhanauri. The latter was found to be 3.55 inches, which is quite low. Besides, the Penman formula is lengthy and involves laborious calculations.

TABLE 3(b)
 Consumptive use and irrigation requirements, I , for the growing season of wheat at Dhanauri by Penman method

Year	Consumptive use, U , in inches	Rainfall, R , in inches	$I = (U - R)/E$ in inches
1956-57	8.07	5.33	3.91
1957-58	8.25	3.53	6.71
1960-61	9.21	9.57	0
Mean	8.51	6.14	3.55

2.5. Thornthwaite formula, evolved by C. W. Thornthwaite of the United States Weather Bureau, was applied next.^{4, 7} It is assumed that an exponential relationship exists between mean monthly temperature and mean monthly con-

sumptive use. Using the standard nomograph, values of heat index were derived as per Table 4(a). These values, when corrected as per Table 4(b), gave the

TABLE 4(a)
Calculations of consumptive use during the growing season of wheat at Dhanauri by Thornthwaite method

Year	Month	t in °C	Heat index $i = (t/5) 1.514$	Potential monthly evapo-transpiration in cm.
1956-57	November	18.33	7.15	9.5
	December	15.11	5.32	8
	January	13.61	4.56	7
	February	14.22	4.88	7.5
1957-58	November	18.00	6.96	9.5
	December	14.39	4.95	7.5
	January	14.50	5.02	7.5
	February	15.22	5.39	8
1960-61	November	18.00	6.96	9
	December	15.06	5.32	8
	January	14.06	4.79	7.5
	February	13.72	4.63	7.5

TABLE 4(b)
Corrected evapotranspiration for the growing season of wheat at Dhanauri by Thornthwaite method

Year	Month	Uncorrected evapotranspiration in cm.	Corrected evapotranspiration in cm.
1956-57	November	9.5	8.46
	December	8	7.04
	January	7	6.30
	February	7.5	6.53
Total 28.33 or 11.15 inches			
1957-58	November	9.5	8.45
	December	7.5	6.60
	January	7.5	6.75
	February	8	6.96
Total 28.76 or 11.32 inches			
1960-61	November	9	8.01
	December	8	7.04
	January	7.5	6.75
	February	7.5	6.53
Total 28.33 or 11.15 inches			

monthly consumptive use in centimeters. The corrections were based upon a table deduced for making allowance for possible duration of sunlight expressed in units of 30 days of 12 hours each. For Dhanauri with a latitude of 30°N, the correction factors were found to be 0.89, 0.88, 0.90 and 0.87 for the months of November to February respectively. Table 4(c) shows the computed consumptive use and irrigation requirements during the growing season of wheat at Dhanauri. The latter was found to be 7.23 inches, which is rather low as compared to the experimental figure of 8.50 inches. As before, E was taken to be 70%.

TABLE 4(c)
Consumptive use or evapotranspiration and irrigation requirements, I, during
the growing season of wheat at Dhanauri by Thornthwaite method

Year	Consumptive use, U, in inches	Rainfall, R, in inches	I = (U - R)/E in inches
1956-57	11.15	5.33	8.31
1957-58	11.32	3.53	11.13
1960-61	11.15	9.57	2.26
Mean	11.21	6.14	7.23

2.6. The next formula applied was that of C. H. Hargreaves, Irrigation Advisor, Rio de Janeiro, Brazil.^{5,7} This method is based upon two assumptions: (i) That evaporation of water is a physical process and can be computed; (ii) That an empirical relationship exists between computed evaporation and consumptive use of water by various crops. The formula is as follows :—

$$2.6.1. \quad e = d(0.38 - 0.0038h)(t - 32),$$

where e = monthly evaporation in inches,

d = a monthly daytime coefficient dependent upon latitude,

h = mean monthly relative humidity at noon,

t = mean monthly temperature in °F.

2.6.2. Table 5(a) gives computations of monthly evaporation, ϵ , during the growing season of wheat at Dhanauri by Hargreave's method. In Table 5(b) are given the values of E_1 which is the total evaporation during the growing season. This multiplied by K which is the crop coefficient or the ratio of consumptive use to evaporation and is assumed as 0.70 as before gives the value of consumptive use, wherefrom irrigation requirements were worked out, taking E as 70%.

TABLE 5(a)

Computations of monthly evaporation during the growing season of wheat at Dhanauri by Hargreave's method

Month	Mean rel. humidity at noon%	Mean temp. °F	d	0.38—0.0038 \times	$t - 32$	$\epsilon = (4) \times (5)$	$\times (6)$	
						1	2	3
1956-57	November	45.2	65.0	0.66	0.20824	33.0		5.910
	December	43.2	59.2	0.86	0.21584	27.2		5.049
	January	61.3	56.5	0.88	0.14706	24.5		3.171
	February	33.5	57.6	0.94	0.25270	25.6		6.081
1957-58	November	41.6	64.4	0.86	0.22192	32.4		6.184
	December	58.3	57.9	0.86	0.15846	25.9		3.530
	January	48.2	58.1	0.88	0.19684	26.1		4.521
	February	31.5	59.4	0.94	0.26030	27.4		6.704
1960-61	November	25.0	64.4	0.86	0.27360	32.4		7.624
	December	31.0	59.1	0.86	0.26220	27.1		6.111
	January	53.1	57.3	0.88	0.17822	25.3		3.968
	February	40.0	56.7	0.94	0.22800	24.7		5.294

TABLE 5(b)

Consumptive use, U, calculated from evaporation, E_1 during the growing season, and irrigation requirements, I, for wheat at Dhanauri by Hargreave's method

Year	Evaporation, E_1 , in inches	Crop co-efficient, K	Consumptive use, $U = KE_1$, in inches	Rainfall, R, in inches	$I = (U - R)/E$ in inches
1956-57	20.21	0.70	14.15	5.33	12.60
1957-58	20.94	0.70	14.66	3.53	15.90
1960-61	22.99	0.70	16.10	9.57	9.31
Mean	21.38	0.70	14.97	6.14	12.61

2.6.3. It is clear that the mean consumptive use arrived at by Hargreave's method is rather high as compared to the experimental figure, being 12.61 inches against 8.50 increase for the latter.

2.7. The last approach was that of Van Bavel of the Virginia Agricultural Experiment Station, Blacksburg, Virginia U. S. A., in which the mean daily evapotranspiration is calculated by the number of drought-days in a month for the growing season of a particular crop.^{6,7} Table 6(a) gives the number of drought days every month during the growing season of wheat at Dhanauri. Table 6(b) gives mean daily evapotranspiration for the same period worked out by Penman formula. Consumptive use is the total evapotranspiration during the growing season. Irrigation requirements calculated by Van Bavel method are shown in Table 6(c), assuming E to be 70%. It is to be seen that the calculated figure of 2.76 inches is much lower than the experimental figure of 8.50 inches.

TABLE 6(a)
Number of drought days during the growing season of wheat at Dhanauri

Year	November	December	January	February
1956-57	28	31	21	27
1957-58	28	26	27	25
1960-61	30	30	25	23
Mean	29	29	24	25

TABLE 6(b)
Mean daily evapotranspiration in inches monthwise during the growing season of wheat at Dhanauri

Year	November	December	January	February
1956-57	0.071	0.053	0.051	0.097
1957-58	0.071	0.048	0.061	0.098
1960-61	0.072	0.065	0.062	0.122
Mean	0.072	0.055	0.055	0.106

TABLE 6(c)
Monthly evapotranspiration, consumptive use, U, during the growing season and irrigation requirements, I, in inches by Van Bavel method

Year	Evapotranspiration in inches				Consumptive use, U, in inches	Rainfall, R, in inches	$I = (U - R)/E$ in inches
	November	December	January	February			
1956-57	0.071×28 = 1.99	0.053×31 = 1.64	0.051×21 = 1.07	0.097×27 = 2.62	7.32	5.33	2.84
1957-58	0.071×28 = 1.99	0.048×26 = 1.25	0.061×27 = 1.65	0.098×25 = 2.45	7.34	3.53	5.41
1960-61	0.072×30 = 2.16	0.065×30 = 1.95	0.062×25 = 1.55	0.122×23 = 2.81	8.47	9.57	0
	Mean				7.70	6.44	2.76

TABLE 7

Consumptive use and irrigation requirements, calculated by different formulae, as also actual irrigation applications in experiments on water requirements of wheat (or experimentally determined figures for irrigation requirements) at Dhanauri in Western U. P. for the years 1956-57, 1957-58 and 1960-61

Formula used	Consumptive use or water requirements in inches, U	Calculated irrigation requirements in inches	Experi- mentally deter- mined irrigation requirements in inches	Remarks	
	1	2	3		4
Lowry-Johnson	19.64	22.83	8.50	1.	I has been calculated from the equation, $I = (U - R)/E$, where R is rainfall in inches and E the irrigation application efficiency which has been assumed as 70%.
Blaney-Criddle	11.96	8.31 (with K=0.70)	8.50		
Penman	8.51	3.55	8.50		
Thornthwaite	11.21	7.23	8.50		
Hargreaves	14.97	12.61	8.50		
Van Bavel	7.71	2.79	8.50	2.	In Lowry-Johnson formula, R is taken as the effective precipitation which is worked out from actual precipitation with the aid of some tables.
				3.	A comparison of columns (3) and (4) gives an idea of the type of agreement between calculated and experimental figures.
				4.	Columns 2, 3, 4 give mean figures for the years 1956-57, 1957-58 and 1960-61.

2·3. A review of the work done on the applicability of various empirical formulae for the assessment of irrigation requirements from climatological data shows that while the Lowry-Johnson and Hargreave's formulae give high figures for irrigation requirements, the results obtained from Penman and Van Bavel formulae are quite low. Only the Blaney-Criddle formula gives a close analogy with experimental figures. Besides, this formula is quite simple. Thornthwaite formula also gives results whose divergence from experimental figures is not quite significant.

3·0. CONCLUSIONS

3·1. Blaney-Criddle formula is indicated to be most suitable for the determination of irrigation requirements from climatological data in view of the accuracy of the results and the simplicity of the calculations involved.

4·0. ACKNOWLEDGMENTS

4·1. The author wishes to record his deep sense of gratitude to Sri S. N. Gupta, Director, Irrigation Research Institute, Roorkee for his generous and valuable help, facilities and permission extended for the publication of this paper. He is thankful to Sarva Sri S. K. Jindal and B. P. Srivastava for their help in the computations and compilation of this paper.

REFERENCES

1. R. L. Lowry, Jr. and A. F. Johnson, "Consumptive Use of Water for Agriculture" Proceedings of the American Society of Civil Engineers, Vol. 107, pp. 1243-1302, 1942.
2. Blaney, H. F. and Criddle, W. D., "Determining Water Requirements in Irrigated Areas from Climatological and Irrigation Data", U. S. Department of Agriculture, SCS-TP-96, August, 1960.
3. Penman, H. L., "Natural Evaporation from Open Water, Bare Soil and Grass", Proceedings of the Royal Society of London, Series A 193:120-145, 1948.
4. G. W. Thornthwaite, "An Approach Towards a Rational Classification of Climate", The Geographical Review, Vol. 88, pp. 55—94 (1948).
5. G. H. Hargreaves, "Irrigation Requirements based on Climatic Data", Paper 1105, IR-3, Journal of the Irrigation and Drainage Division, Proceedings of the American Society of Civil Engineers, November, 1956.
6. "Agricultural Drought in Virginia", Technical Bulletin 128, April 1957, Virginia Agricultural Experiment Station, Blacksburg, Virginia.
7. W. D. Criddle, "Methods of Computing Consumptive Use of Water", Journal of the Irrigation and Drainage Division, Proceedings of the American Society of Civil Engineers, January, 1958.

EFFECT OF DIFFERENT ORGANIC MATERIALS AND PHOSPHATES ON THE YIELD OF PADDY GRAIN AND STRAW IN FIELD TRIALS.

By

N. R. DHAR and G. SINGH

Sheila Dhar Institute of Soil Science, University of Allahabad, Allahabad.

[Received on 14th October, 1963.]

ABSTRACT

Field trials carried on at Anapur (Allahabad) using wheat straw, *Kans* or sunhemp either singly at 10 tons per acre or when mixed with Tata basic slag at the rate of 50 lbs. P_2O_5 per acre show highly significant increased yield of paddy grain and straw, phosphated wheat straw produces the best yield. Moreover there is much greater increase in the humus capital and fertility of the soil when these organic substances are ploughed in directly in the soil than in the addition of composts obtained from these materials.

In this paper we have studied the effect of different organic materials like wheat straw, *kans* (*Saccharum Spontaneum*) and *sunhemp* (*Crotalaria Juncia*) alone and in conjunction with Tata basic slag on the yield of paddy grain and straw in fields.

METHODS AND MATERIALS

The field trials were carried out at Anapur (Allahabad), U. P. The area of the land selected for these experiments was as uniform as possible and this minimised the effect of soil fertility differences between the plots. The experience of the resident farmers was utilized in selection of the site. Soil samples were taken one from the different layers and from different spots upto a depth of 6" in order to determine the uniformity of the soil of the field. The soil was of alluvial type in which crops were continuously grown for a number of years.

Details of layout :—

(A) *Treatments*

1. Soil alone (control).
2. Soil + Wheat straw.
3. Soil + Wheat straw + phosphate.
4. Soil + *kans* straw.
5. Soil + *kans* straw + phosphate.
6. Soil + *sunhemp*.
7. Soil + *sunhemp* + phosphate.

(B) *Design of the experiment.*

(I) Randomised block layout.

(II) Number of treatments = 7.

(III) Number of Replications = 6

(IV) Number of plots = 42

(C) Area of the size of the plot = 1/60th of an acre (33 ft. \times 22 ft.)

(D) Rate of addition of the amendment per acre :—

(i) Organic material = 10 tons

(ii) Phosphate (as Tata basic slag) = 50 lbs.

(E) Place : Anapur (Allahabad district).

(F) Period of decomposition of the amendments and fertilizers in plots—
from 20th April to 2nd July, 1961.

(G) Number of ploughing during decomposition = 6

(H) Soil samples were taken before transplanting on 26th June, 1961.

(I) Soil samples were taken after harvesting of the crop on 4th October, 1961.

(J) Date of transplanting — 3rd July, 1961.

(K) Date of harvesting — 4th October, 1961.

Canal water was used for irrigation for the paddy crop.

Chemical composition of energy materials (oven dried) %

Constituents		Wheat straw	Kans	Sunhemp	Soil
Loss on ignition	...	91.87	90.51	89.45	3.86
Ash	...	8.13	9.49	10.55	96.14
HCl insoluble	...	4.89	5.81	4.88	70.51
Sesquioxide	...	0.9261	0.8670	0.7246	11.1821
Fe_2O_3	...	0.4123	0.3642	0.2946	4.1342
CaO	...	0.7751	0.6861	1.2024	0.9871
P_2O_5	...	0.5623	0.5224	0.3277	0.0787
K_2O	...	0.8662	0.8572	0.7462	0.9782
MgO	...	0.5015	0.4831	0.4362	0.5583
Available P_2O_5 (1% citric acid soln.)	0.0162
Total carbon	...	39.82	37.65	22.65	0.5475
Total nitrogen	...	0.6433	0.6217	0.8625	0.0558
$\text{NH}_3 - \text{N}$	0.0048
$\text{NO}_3 - \text{N}$	0.0063
C/N ratio	...	61.8	60.7	26.2	10.8

(l) Tata basic slag contains 7.57% P_2O_5 .

Composition of soil (%) before paddy transplantation

Constituents	Soil alone (control)	Soil + wheat straw (10 tons/acre)	Soil + wheat straw (10 tons/acre + P_2O_5 as T.B.S. (50 lbs/acre)	Soil + Kans straw (10 tons/acre + P_2O_5 as T.B.S. (50 lbs/acre)	Soil + sunhemp straw (10 tons/acre) + P_2O_5 as T.B.S. (50 lbs/acre)	Soil + sunhemp straw (10 tons/acre) + P_2O_5 as T.B.S. (50 lbs/acre)
Sesquioxide	...	11.1821	11.2132	11.4212	11.1952	11.3516
Fe_2O_3	...	4.1342	4.1521	3.2623	4.1426	4.2152
CaO	...	0.9871	1.1231	1.4263	1.0985	1.3545
P_2O_5	...	0.0787	0.0823	0.2534	0.0809	0.2262
Av. P_2O_5 11% citric acid soln.	0.0162	0.0213	0.0625	0.0196	0.0526	0.0799
K_2O	...	0.9782	1.0152	1.1274	1.0095	1.0973
MgO	...	0.5583	0.5926	0.6265	0.5626	0.6083
Total carbon	...	0.5468	0.8243	0.6476	0.8077	0.6621
Total nitrogen	...	0.0554	0.0942	0.1272	0.0884	0.1154
NH_3-N	...	0.0043	0.0135	0.0157	0.0126	0.0148
NO_3-N	...	0.0064	0.0154	0.0265	0.0148	0.0225
C/N ratio	...	10.8	8.7	5.0	9.1	5.7
					7.9	5.6

Composition of soil (%) after harvesting of paddy crop

Sesquioxide	...	11·1552	11·1842	11·3042	11·1726	11·2055	11·1652	11·1894
Fe ₂ O ₃	...	3·6641	3·9652	4·0527	3·8825	3·9976	3·7263	3·8762
CaO	...	0·9682	1·0045	1·2652	0·9959	1·1246	0·9866	1·1065
P ₂ O ₅	...	0·0762	0·0784	0·2267	0·0796	0·2076	0·0786	0·1885
Av. P ₂ O ₅ (1% citric acid solt).	...	0·0142	0·0246	0·0675	0·0214	0·0566	0·0208	0·0539
K ₂ O	...	0·9552	0·9862	1·0087	0·9826	1·0076	0·9845	1·0065
MgO	...	0·5463	0·5615	0·5847	0·5602	0·5672	0·5596	0·5648
Total carbon	...	0·5436	0·6842	0·5865	0·6687	0·6056	0·6078	0·5606
Total nitrogen	...	0·0543	0·0836	0·1027	0·0805	0·0943	0·0783	0·0874
NH ₃ - N	..	0·0042	0·0146	0·0164	0·0138	0·0156	0·0132	0·0144
NO ₃ - N	...	0·0058	0·0167	0·0272	0·0158	0·0233	0·0146	0·0206
C/N ratio	...	10·0	8·1	5·7	8·3	6·4	8·1	6·4

Yield of paddy grain in Kgs.

Treatments	B L O C K S					Total
	1	2	3	4	5	
Soil alone (control) ...	11.50	12.25	10.75	11.00	13.00	10.25
Soil + wheat straw (10 tons/acre).	18.00	17.25	19.50	16.50	18.50	18.25
Soil + wheat straw (10 tons/acre) + P_2O_5 as T. B. S. (50 lbs/acre).	23.25	22.75	23.50	24.50	21.50	23.50
Soil + kans straw (10 tons/acre) + P_2O_5 as T. B. S. (50 lbs/acre).	16.75	15.50	16.25	17.75	15.00	16.00
Soil + kans straw (10 tons/acre) + P_2O_5 as T. B. S. (50 lbs/acre).	21.75	21.25	22.25	22.75	20.50	21.25
Soil + sunhemp (10 tons/acre).	15.50	14.75	16.75	15.25	15.75	16.00
Soil + sunhemp (10 tons/acre) + P_2O_5 as T. B. S. (50 lbs/acre).	18.75	19.25	17.50	18.50	19.50	18.50
Total ...	125.50	123.00	126.50	126.25	123.75	123.75
						748.75

Analysis of variance for the yield of paddy grain

Sources of variation	D. F.	S. S.	M. S.	Calculated F from table		Level of significance
				1%	5%	
Blocks ...	5	1.5611	0.3122	0.05	3.70	2.53
Treatments ...	6	382.4465	63.7410	10.4	3.47	2.42
Error ...	30	183.3035	6.1101
Total ...	41	567.3111	13.8363

Yield of paddy straw in Kgrns

Treatments	B L O C K S						Total
	1	2	3	4	5	6	
Soil alone (control) ...	30	29	28	25	29	27	168
Soil + wheat straw (10 tons/acre).	52	48	50	47	53	51	301
Soil + wheat straw (10 tons/acre) + P_2O_5 as T. B. S. (50 lbs/acre).	65	62	67	63	68	64	389
Soil + kans straw (10 tons/acre).	45	47	48	46	44	45	275
Soil + kans straw (10 tons/acre) + P_2O_5 as T. B. S. (50 lbs/acre).	60	63	59	64	62	60	368
Soil + sunhemp (10 tons/acre).	42	43	39	40	44	42	250
Soil + sunhemp (10 tons/acre) + P_2O_5 as T. B. S. (50 lbs/acre).	54	53	55	56	52	51	321
Total ...	348	345	346	341	352	340	2072

Analysis of variance for the yield of paddy straw

Source of variance	D. F.	S. S.	M. S.	Calculated F	F. from table		Level of significance
					1%	5%	
Blocks 5	14·2	2·84	0·22	3·70	2·53	Yield is highly significant
Treatments ...	6	5304·0	884·0	69·0	3·47	2·42	...
Error ...	30	386·8	12·8
Total ...	41	5705·0	139·1

DISCUSSION

From the foregoing results it is evident that by the addition of different organic materials like wheat straw, *kans* straw and sunhemp (as green manure) at the rate of 10 ton/acre to the field, much better results were obtained than in the control soil. A good increase in the yield of paddy grain and straw was obtained. Moreover, when phosphate was incorporated with these organic materials at the rate of 50 lbs per acre of P_2O_5 as Tata basic slag, much better results were obtained than the treatments in which phosphate was not added. The effect of different phosphated organic materials on the yeid of paddy grain were in the following order :

Phosphated wheat straw > Phosphated *Kans* straw > and phosphated sunhemp.

The same order in the yield of paddy grain and straw was also observed when only organic materials were added at the rate of 10 tons per acre to the field.

It has also been observed in these field trials that there is greater increase in the yield of paddy grain and straw when organic materials are incorporated with phosphate than without phosphate. These remarkable differences between phosphatated organic materials and the unphosphated ones in the yield of paddy grain and straw may be due to the presence of a higher amount of total nitrogen and phosphate and available nitrogen and phosphate. As it has been observed from the analysis of soil after the decomposition of organic materials and before the transplantation of paddy planis, the plots which were treated with organic materials and phosphate, contained greater amount of total nitrogen, available nitrogen, and available phosphate than the plots which were treated without phosphate.

Many other workers such as Dhar (1), Peevy and Norman (2), Dhar and Gaur (3), Cooper (4), Eden (5), have also reported that by the addition of phosphates to the organic matter, much better results are obtained than with organic matter alone.

In the field trials, the plot which have been treated with wheat straw alone and a mixture of wheat straw and phosphate, highest yields of paddy grain and straw were obtained. It seems, therefore, that the addition of wheat straw alone, and a mixture of wheat straw and phosphate is better out of all the treatments. The chief cause of this higher yield may be due to the presence of greater amounts of lignin in case of wheat straw than in that of *kans* straw and also sunhemp, because, due to the presence of lignin which forms stable ligno-protein, the loss of nitrogen in the soil is decreased.

In addition to the nitrogen content, other minerals were also greater in wheat straw than in the *kans* straw and sunhemp treated plots. The lowest yield was obtained in sunhemp treated plots, leaving the 'control'. Sunhemp at its green stage contains less amount of carbonaceous material. Therefore, it appears that a certain amount of lignin present in the composting of plant materials is helpful in maintaining and improving the nitrogen status of the soil in which loss of nitrogen can be minimised.

We have also observed in our field trials that by the driect addition of organic materials and phosphate to the soil, there is much greater increase in the humus capital of the soil, because, the organic substances which were added

directly to the field, have a higher C/N ratio than the composted organic substances. Therefore, there are more chances for the fixation of atmospheric nitrogen when added directly to the field instead of the composting of organic substances in heaps because in heaps much of the nitrogen is lost.

From the foregoing field trials we have come to the conclusion that the direct application of organic materials along with phosphate ploughed in the soil, certainly increases the land fertility considerably and increased yields are obtained.

REFERENCES

1. Dhar, N. R., Presi. Address to the 48th Indian Sc. Congr., Roorkee, 1961, p. 11.
2. Peevy, W. J. & Norman, A. G., *Soil Sci.*, 65, 209-226 (1948).
3. Gaur, A. C., D. Phil, thesis, University of Allahabad, Allahabad (1967).
4. Cooper, H. R., *Mem. Ind. Tea. Association*, 6 (1939).
5. Eden, T. *Tea Quart. Ceylon*, 10, 113.

FIXATION OF ATMOSPHERIC NITROGEN IN THE INCUBATION OF ORGANIC MATERIALS HELPED BY PHOSPHATES

By

N. R. DHAR and G. SINGH

Sheila Dhar Institute of Soil Science, University of Allahabad, Allahabad.

[Received on 14th October, 1963.]

ABSTRACT

In the slow oxidation of paddy straw, wheat straw, barley straw, oat straw, water hyacinth, lucerne straw, napier grass straw, castor cake, ground nut cake and *Kans* straw kept in an incubator at 37°C, there is marked oxidation of the carbonaceous compounds after 100 days and fixation of atmospheric nitrogen especially in presence of superphosphate, Tata basic slag and Kulti basic slag in the cases of wheat straw, barley straw, oat straw, water hyacinth, lucerne straw, napier grass straw and *Kans* straw. But there was marked loss of nitrogen with castor cake and ground nut cake in the nitrification of the proteins present in these cakes, the loss of nitrogen is checked by adding phosphates.

A number of methods for the preparation of composts have been advocated. In a majority of these methods, except slight modification in technique, the principles have practically remained the same as enumerated by Hutchinson and Richards (1). Various mixture of inorganic nitrogenous compounds and other sources of nitrogen have also been used bringing about rapid decomposition of organic matter. As Albrecht and Poirot 1927 (2) suggested that the use of a mixture of 45% ammonium sulphate, 15% superphosphate and 40% lime stone to be applied at the rate of 150 lbs per ton of wheat straw, resulted in a good manure in 3 to 5 months. Gadgil (3) used a mixture of ammonium sulphate and calcium carbonate. In this way different workers have used different sources of available nitrogen for rapid decomposition. We have used phosphates instead of nitrogenous fertilizers in studying the decomposition of organic materials.

The present investigations were undertaken to study systematically the composting of various kinds of organic matter in incubation experiments at 37°C.

EXPERIMENTAL

The set of experiments was carried out in weighed wide mouthed bottles of equal size and were kept at 37°C in an electric incubator for 100 days. 25 gms of well powdered organic substances were added in different bottles. 0.5% P_2O_5 was mixed as Tata basic slag, superphosphate, and Kulti basic slag in each of the organic substances separately, leaving one of each organic substances without phosphate.

The moisture was maintained at 50% level. The bottles were stirred thrice in a week. After 100 days the bottles were removed and weighed. The whole material was dried and crushed in a pestle and mortar to a powdery mass to pass through a 80 mesh sieve. The analysis was made for total carbon and total nitrogen.

Analysis of following organic materials

		Total carbon %	Total nitrogen %	C/N ratio
Paddy straw	...	31.50	0.4900	64.2
Wheat straw	...	32.60	0.6541	50.1
Barley straw	...	33.65	0.6623	50.9
Oat straw	...	21.15	0.5213	40.6
Water hyacinth (Eichornia Crassipes)		32.55	1.3125	24.8
Lucerne straw	...	33.60	0.6615	50.9
Napier grass straw	...	34.65	0.4952	70.7
Castor cake (Ricinus communis)	...	43.05	4.7950	8.9
Ground nut cake (Anachis hypoaea)		39.30	5.7750	6.8
Kans straw	...	39.86	0.7046	56.9

Analysis of different phosphatic materials.

	Superphosphate %	Tata basic slag %	Kulti basic slag %
Silica	44.82	33.56	31.00
Sesquioxide	28.31
Fe_2O_3	...	17.79	7.85
Al_2O_3	15.44
Total P_2O_5	16.52	7.57	7.94
Available P_2O_5	14.12	4.21	3.95
Total CaO	36.18	34.52	31.77
Total K_2O	0.24	...	0.59
Total MgO	0.26	5.25	3.05

Incubation temperature 37°C

Treatments	Initial carbon in mgms	Total carbon after 100 days in mgms	Initial nitrogen in mgms	Total nitrogen after 100 days in mgms	Loss (-) or gain (+) of N ₂ in mgms.
25 gms of paddy straw + 50% moisture.	7875·0	3172·5	122·5	228·2	105·7
25 gms of paddy straw + 0·5% P ₂ O ₅ as superphosphate.	7875·0	2777·5	122·5	253·9	131·4
25 gms of paddy straw + 0·5% P ₂ O ₅ as Tata basic slag.	7875·0	2350·0	122·5	272·5	150·0
25 gms of paddy straw + 0·5% P ₂ O ₅ as Kulti basic slag.	7875·0	2570·0	122·5	251·6	129·1
25 gms of wheat straw + 50% moisture.	8150·0	3220·0	163·5	311·7	148·2
25 gms of wheat straw + 0·5% P ₂ O ₅ as superphosphate.	8150·0	2572·5	163·5	344·0	180·5
25 gms of wheat straw + 0·5% P ₂ O ₅ as Tata basic slag.	8150·0	2095·0	163·5	385·5	222·0
25 gms of wheat straw + 0·5% P ₂ O ₅ as Kulti basic slag.	8150·0	2255·0	163·5	339·4	175·9
25 gms of barley straw + 50% moisture.	8412·5	3147·5	165·5	313·7	148·2
25 gms of barley straw + 0·5% P ₂ O ₅ as superphosphate.	8412·5	2482·5	165·5	349·5	184·0
25 gms of barley straw + 0·5% P ₂ O ₅ as Tata basic slag.	8412·5	2090·0	165·5	376·3	210·8
25 gms of barley straw + 0·5% P ₂ O ₅ as Kulti basic slag.	8412·5	2272·5	165·5	345·2	179·7
25 gms of oat straw + 50% moisture.	5287·5	2242·5	130·3	245·8	115·5
25 gms of oat straw + 0·5% P ₂ O ₅ as superphosphate.	5287·5	1822·5	130·3	271·4	141·1
25 gms of oat straw + 0·5% P ₂ O ₅ as Tata basic slag.	5287·5	1502·5	130·3	292·6	162·3

Incubation temperature 37°C

Treatment	Initial carbon in mgms	Total carbon after 100 days in mgms	Initial nitrogen in mgms	Total nitrogen after 100 day in mgms	Loss (-) or gain (+) of N ₂ in mgms
25 gms of oat straw + 0·5% P ₂ O ₅ as Kulti basic slag.	5287·5	1622·5	130·3	268·8	138·5
25 gms of water hyacinth + 50% moisture.	8162·5	3540·0	328·1	554·1	226·0
25 gms of water hyacinth + 0·5% P ₂ O ₅ as superphosphate.	8162·5	2955·0	328·1	619·7	291·6
25 gms of water hyacinth + 0·5% P ₂ O ₅ as Tata basic slag.	8162·5	2650·0	328·1	706·7	378·6
25 gms of water hyacinth + 0·5% P ₂ O ₅ as Kulti basic slag.	8162·5	2772·5	328·1	611·9	283·8
25 gms of Lucerne straw + 50% moisture.	8400·0	2932·5	165·3	318·3	153·0
25 gms of Lucerne straw + 0·5% P ₂ O ₅ as superphosphate.	8400·0	2587·5	165·3	351·2	185·9
25 gms of Lucerne straw + 0·5% P ₂ O ₅ as Tata basic slag.	8400·0	2175·0	165·3	379·0	213·7
25 gms of Lucerne straw + 0·5% P ₂ O ₅ as Kulti basic slag.	8400·0	2362·5	165·3	346·7	181·4
25 gms of napier grass straw + 0·5% moisture.	8662·5	3535·0	123·8	232·0	108·2
25 gms of napier grass straw + 0·5% P ₂ O ₅ as superphosphate.	8662·5	2910·0	123·8	257·2	133·4
25 gms of napier grass straw + 0·5% P ₂ O ₅ as Tata basic slag.	8662·5	2397·5	123·8	276·6	152·8
25 gms of napier grass straw + 0·5% P ₂ O ₅ as Kulti basic slag.	8662·5	2592·5	123·8	253·4	126·6
25 gms of castor cake + 50% moisture.	10762·5	5102·5	1198·7	1004·6	-194·1
25 gms of castor cake + 0·5% P ₂ O ₅ as superphosphate.	10762·5	4507·5	1198·7	-1024·9	-173·8

Incubation temperature 37°C

Treatment	Initial carbon in mgms	Total carbon after 100 days in mgms.	Initial nitrogen in mgms	Total nitrogen after 100 days in mgms	Loss (-) or gain (+) of N ₂ in gms
25 gms of castor cake + 0.5% P ₂ O ₅ as Tata basic slag.	10762.5	3855.0	1198.7	-1035.7	-163.0
25 gms of castor cake + 0.5% P ₂ O ₅ as Kulti basic slag.	10762.5	4442.5	1198.7	-1011.8	-186.9
25 gms of ground nut cake + 50% moisture.	9825.0	5052.5	1443.7	-1175.2	-268.5
25 gms of ground nut cake + 0.5% P ₂ O ₅ as super-phosphate.	9825.0	4360.0	1443.7	-1205.5	-238.2
25 gms of ground nut cake + 0.5% P ₂ O ₅ as Tata basic slag.	9825.0	3842.5	1443.7	-1221.4	-222.3
25 gms of ground nut cake + 2.5% P ₂ O ₅ as Kulti basic slag.	9825.0	4002.5	1443.7	-1196.9	-246.8
25 gms of kans straw + 50% moisture.	9965.0	3637.5	176.1	332.3	156.2
25 gms of kans straw + 0.5% P ₂ O ₅ as super-phosphate.	9965.0	3320.0	176.1	369.2	193.1
25 gms of kans straw + 0.5% P ₂ O ₅ as Tata basic slag.	9965.0	2972.5	176.1	384.7	208.6
26 gms of kans straw + 0.5% P ₂ O ₅ as Kulti basic slag.	9965.0	3132.5	176.1	361.3	185.2

DISCUSSION

A perusal of the incubation experimental results recorded in the above tables, show that there is an appreciable oxidation of carbon and an increase in the total nitrogen of the system, when different organic substances were mixed without phosphates. It is further observed that when to these organic substances, phosphates are added, there is a copious loss of carbon and an increase in total nitrogen is greatly enhanced. When these organic substances were treated without phosphates at 37°C, a fair amount of carbon is lost, i.e., from 48·6% to 64·5% lowest in the case of ground nut cake and highest in the case of lucerne straw respectively. There is also a greater loss of carbon, in the presence of phosphates at 37°C (incubation temperature), the highest loss of carbon was found in case of lucerne straw i.e. 72·4% along with Tata basic slag, and lowest loss of carbon was found in case of ground nut cake i.e. 54·3% along with superphosphate, which is acidic and retards oxidation of organic matter.

The experimental results also indicate that there is considerable fixation of atmospheric nitrogen with and without different phosphates during the incubation at 37°C, but greater amount of nitrogen was fixed with phosphates than without phosphates. Without phosphates the fixation of atmospheric nitrogen in different organic substances varied from 65·3% to 92·6% lowest in the case of cow dung and highest in the case of lucerne straw when compared to the total nitrogen present in the system within a period of 100 days' incubation. While in the case of phosphated different organic substances the fixation of atmospheric nitrogen was greater and it varied from 84·6% to 135·8% lowest in the case of cow dung when treated with Kulti basic slag and highest in the case of wheat straw, when treated with Tata basic slag respectively, within the period of 100 days incubated at 37°C. It has also been observed that there is loss of nitrogen, instead of nitrogen fixation when the amount of initial nitrogen is large in the system, even in the presence of phosphates as in the case of ground nut cake and castor cake. The highest loss has been observed 15·6% in case of castor cake and 17·1% in case of ground nut cake, when mixed with Kulti basic slag within period of 100 days incubation. In general the fixation of atmospheric nitrogen was greater in presence of phosphates than in the absence of phosphates, and also greater conservation of nitrogen was achieved in presence of phosphates than in absence,

It has been observed that when the amount of nitrogen is small in the system, an appreciable amount of nitrogen fixation has been observed, and when the amount of nitrogen is large, there is always a copious loss of nitrogen. As in the case of castor cake and ground nut cake, a loss of nitrogen is observed. Due to presence of urea, uric acid etc. which nitrify easily, the amount of nitrogen fixed in cowdung and horse dung is less when compared with wheat straw and barley straw containing no available nitrogen in the beginning.

In the experiments of Hutchinson and Richards (1) with straw and urine, a large amount of urine was used and there was a copious loss of nitrogen after incubation at 26°C and 36°C. Dhar and Biswas (4) have found that when oil cakes are composted alone, there is appreciable amount of loss of nitrogen. Srivastava, Chaturvedi and Rao (5) have reported, during the composting of cane trash and press mud, losses of nitrogen from 20 to 50%. It seems, therefore, if the nitrogen content of the system is high in the beginning, it is always lost subsequently.

Hutchinson and Richards (1) could not explain the nitrogen gain in their experiments with straw alone. Dhar (6) in his paper "The role of organic matter in soil fertility" was the first to explain, this increase of nitrogen in the incubation of straw alone from the view point of atmospheric nitrogen fixation caused by the liberation of energy evolved in the slow oxidation of cellulose and lignin.

It has also been observed in these experiments that the organic materials, which are rich in lignin had a higher fixation of nitrogen than with organic substances which are poor in lignin content, as in the case of composting of wheat straw, barley straw etc. higher amount of nitrogen was fixed. Therefore, it appears that due to presence of lignin, which can form stable ligno-proteins, the loss of nitrogen in composting is decreased. Peevy and Norman (7) have observed, that the soil receiving more resisting materials like lignins had a higher content of nitrogen. It appears, therefore, that a certain amount of lignin present in the composting of plant materials is helpful in maintaining and improving the nitrogen status of a compost.

Moreover, from our experiments, we have come to the conclusion, that organic matter like wheat straw, leaves and dung can play a vital role in the preservation of nitrogen and fixation of atmospheric nitrogen in the system, and

this processes definitely helped by the addition of different calcium phosphates to the system. All basic slags produced in the Indian steel factories are beneficial in composting.

REFERENCES

1. Hutchinson and Richards, *Jour. Min., Agri., (Gt. Brit.)*, 28, 398-411 (1921).
2. Albrecht, W. A. and Poirot, *Mo. Agri. Expt. Sta. Bull.* 258 (1927).
3. Galgil, V. V., *Agri. and live stock in India*, 7, 711 (1937).
4. Dhar, N. R. and Biswas, N. N., *Proc. Nat. Acad. Sci. India, Sec. A.*, Vol. 17 (1948).
5. Srivastava, R. C., Chaturvedi, H. S. and Rao, K. A. N., *Indian Jour. Agri. Sci.*, 12, 159 (1942).
6. Dhar, N. R., *Presi. Address, Nat. Acad. Sci. India* (1953).
7. Peevy, W. J. and Norman, A. G., *Soil Sci.*, 65, 209-226 (1948).

EFFECT OF DIFFERENT COMPOSTS ON THE YIELD OF BARLEY GRAIN AND STRAW IN POTS

By

N. R. DHAR and G. SINGH

Sheila Dhar Institute of Soil Science, University of Allahabad, Allahabad

[Received on 14th October, 1963]

ABSTRACT

For obtaining greater yields of barley grains and straw phosphated municipal rubbish, is much better than the unphosphated municipal rubbish or leaf compost. The amounts of total and available nitrogen, total and available phosphate are much greater in phosphated municipal waste than in the unphosphated municipal waste.

Several laboratory methods have been developed for determining the manurial requirements of soils, but, none is able to answer the important practical question of just what manure and what quantity should be applied to a given soil to obtain the maximum yield of certain crops under field conditions. This could not be expected, for the supply of nutrients is only one of the many factors that affect plant growth. The fact remains, however, that certain chemical and biological tests aid in giving us a better understanding of the possible supply of nutrients in the soil and permit the determination of the possible manurial needs of such soils. Pot test is one of the methods which comes under biological tests.

Pot tests, with many modifications, have been used by various investigators for determining the manurial requirements of the soils. Essentially, these tests consist in filling a number of pots with a soil material and in adding to it various fertilizers and manures. The need for fertilizers and manures is indicated by the growth of the crop, by the amount of dry matter produced or by analysis of plant ash. These tests are usually conducted under green house or laboratory conditions and permit the control of moisture supply, temperature and other factors that cannot be controlled in conducting field trials. Pot tests are ranking second to field experiments for determining the manurial or fertilizer needs of a soil.

Hence in view of the above facts, we have carried out some pot experiments in studying the effect of different composts prepared by us on the yield of barley grain and straw.

METHODS AND MATERIALS

For pot experiments, the soil was collected from the Sheila Dhar Institute garden. It was dried, well powdered and thoroughly mixed. 10 Lbs of this soil were filled up in each earthen pot. To these earthen pots well decomposed leaf compost, phosphated and unphosphated municipal rubbish were properly mixed and added at the rate of 10 tons/acre and 5 tons/acre. Replication was carried out 6 times for each treatment. After mixing it uniform, 8 seeds of barley grain were sown in each earthen pot and they were covered with a wire net to avoid birds and other harmful insects, and a proper care was taken. After an interval of 15 days, sufficient amount of distilled water was added in order to maintain the suitable moisture for the barley crop.

The following treatments were undertaken :

1. Phosphated municipal rubbish	5 tons/acre
2. " " "	10 tons/acre
3. Leaf compost	5 tons/acre
4. " "	10 tons/acre
5. Unphosphated municipal rubbish	5 tons/acre
6. " "	10 tons/acre
7. Soil alone (control)		
Date of sowing	20th November, 1960
Date of harvesting	29th March, 1961
No. of seeds in each pots	8
No. of treatments	7
No. of replication	6
Total no. of earthen pots	42

TABLE I
Analysis of materials

	Leaf compost %	Posphated municipal rubbish %	Unphospha- ted municipal rubbish %	Soil %
Loss on ignition	21.91	6.24	10.65
Ash	78.09	93.76	89.35
HCl insoluble	60.34	71.22	75.00
Sesquioxide	9.28	10.23	10.06
Fe ₂ O ₃	2.87	3.66	4.72
P ₂ O ₅	0.9216	1.2156	0.8525
Available P ₂ O ₅ 1% citric acid soln.	0.2857	0.3650	0.2453
CaO	2.6542	3.2162	1.8425
K ₂ O	1.8622	0.8054	0.7521
MgO	0.2852	0.2615	0.2506
Total Carbon	8.69	4.16	6.27
Total nitrogen	1.45	1.25	0.8242
NH ₃ — N	0.0754	0.0542	0.0268
NO ₃ — N	0.1449	0.1155	0.0506
Total available N ₂ over total nitrogen	15.2	13.5	9.4
C/N ratio	5.9	3.3	7.6
				10.2

TABLE 2
Composition of soil after mixing different composts

	TREATMENTS						
10 lbs soil + 52 gms phosphated municipal rubbish							
10 lbs soil + 26 gms phosphated municipal rubbish							
10 lbs soil + 52 gms leaf compost							
10 lbs soil + 26 gms leaf compost							
10 lbs soil + 52 gms unphosphated municipal rubbish							
10 lbs soil + 26 gms unphosphated municipal rubbish							
10 lbs soil alone							
Sesquioxide %	7.974	7.916	7.964	7.911	7.973	7.915	7.962
Iron oxide %	2.108	2.084	2.110	2.089	2.121	2.092	2.091
Total P ₂ O ₅ %	0.3768	0.3611	0.3735	0.3682	0.3727	0.3678	0.0672
Available P ₂ O ₅ %	0.0869	0.0848	0.0859	0.0843	0.0855	0.0841	0.0337
Total CaO %	0.8901	0.8718	0.8837	0.8686	0.8745	0.8640	0.8634
Total K ₂ O %	0.5753	0.5708	0.5873	0.5767	0.5747	0.5704	0.5727
Total MgO %	0.1675	0.1660	0.1678	0.1662	0.1674	0.1660	0.1665
Total carbon %	0.4670	0.4335	0.5085	0.4593	0.4811	0.4455	0.4146
Total nitrogen %	0.0559	0.0489	0.0581	0.0499	0.0510	0.0463	0.0421
NH ₃ - N %	0.0015	0.0011	0.0017	0.0013	0.0013	0.0011	0.0009
NO ₃ - N %	0.0029	0.0022	0.0032	0.0024	0.0022	0.0019	0.0016
Total available nitrogen %	0.0044	0.0033	0.0049	0.0037	0.0035	0.0030	0.0025
C/N ratio	8.3	8.3	8.7	9.2	9.4	9.6	9.8

TABLE 3
Analysis of soil after harvest of barley crop

Sesquioxide %	7.953	7.907	7.954	7.903	7.965	7.909	7.921
Iron oxide %	2.095	2.076	2.099	2.079	2.112	2.083	2.043
Total P ₂ O ₅ %	0.3752	0.3602	0.3721	0.3674	0.3715	0.2672	0.0666
Available P ₂ O ₅ %	0.0841	0.0825	0.0834	0.0823	0.0827	0.0820	0.0316
Total CaO %	0.8892	0.8711	0.8827	0.8678	0.8739	0.8635	0.8631
Total K ₂ O %	0.5742	0.5699	0.5862	0.5760	0.5739	0.5659	0.5723
Total MgO %	0.1666	0.1654	0.1669	0.1656	0.1667	0.1656	0.1661
Total carbon %	0.4216	0.4092	0.4624	0.4336	0.4435	0.4230	0.4062
Total nitrogen %	0.0541	0.0467	0.0561	0.0480	0.0508	0.0443	0.0417
NH ₃ - N %	0.0014	0.0011	0.0014	0.0012	0.0011	0.0012	0.0008
NO ₃ - N %	0.0026	0.0020	0.0028	0.0022	0.0020	0.0017	0.0016
Total available N %	0.0040	0.0031	0.0042	0.0034	0.0031	0.0029	0.0024
C/N ratio	7.7	8.7	8.2	9.0	8.7	9.5	9.7

TABLE 4
Yield of barley grain in grams
Replication

Treatments	1	2	3	4	5	6	Total
Phosphated M. R. 5 tons/acre	31	28	30	32	30	29	180
Phosphated M. R. 10 tons/acre	40	42	38	45	40	44	249
Leaf compost 5 tons/acre	27	28	27	26	25	24	157
Leaf compost 10 tons/acre	36	38	36	35	38	37	220
Unphosphated M. R. 5 tons/acre	23	20	24	22	19	21	129
Unphosphated M. R. 10 tons/acre	29	32	34	30	33	32	190
Soil alone (control)	7	7	9	8	12	6	49
Total	193	195	198	198	197	193	1174

TABLE 5
Analysis of variance for the yield of barley grain

Source of variation	D. F.	S. S.	M. S.	Calcu- lated F	F from table		Level of signifi- cance
					1%	5%	
Treatments	6	4282.66	713.77	182.5	3.47	2.42	Yield is
Replication	5	4.00	0.8	0.2	3.70	2.57	highly
Error	30	117.34	3.91	—	—	—	signifi-
Total	41	44.04	107.6	—	—	—	cant

TABLE 6
Yield of barley straw in g.s.
Replication

Treatments	1	2	3	4	5	6	Total
Phosphated M. R. 5 tons/acre	45	42	43	46	43	44	263
Phosphated M. R. 10 tons/acre	64	67	63	72	65	69	400
Leaf compost 5 tons/acre	40	41	38	39	37	36	231
Leaf compost 10 tons/acre	55	63	56	54	60	59	347
Unphosphated M. R. 5 tons/acre	33	32	35	34	30	34	198
Unphosphated M. R. 10 tons/acre	48	50	52	49	52	50	301
Soil alone (control)	15	16	18	17	20	12	98
Total	300	311	305	307	307	304	1838

TABLE 7
Analysis of variance for the yield of paddy straw

Source of variation	D. F.	S. S.	M. S.	Calcu- lated F	F from table		Level of signifi- cance
					1%	5%	
Treatments	6	9957.0	1659.5	255.3	3.47	2.42	Highly
Replication	5	13.1	2.6	0.4	3.70	2.53	signifi-
Error	30	197.6	6.5	—	—	—	cant
Total	41	10167.7	—	—	—	—	

DISCUSSION

From the foregoing experimental results, it can be seen that by the addition of different composts, like phosphated municipal rubbish etc and, also, at different rates, i.e. 5 tons/acre and 10 tons/acre, to the soil in pots, definitely better results are obtained than in the 'control'. A good percentage of increase of the yield in grain and straw is obtained in the case of barley crop. The effect of different composts on the yield of barley grains and straw is in the following order :—
Phosphated municipal rubbish→Leaf compost→Unphosphated municipal rubbish.

Swenson, Cole and Sieling (1), Struthers and Sieling (2), Aslander (3), Das (4), and several other workers have shown better crop response by the application of organic manure and phosphates than with the application of phosphates alone in the soil.

Our experiments also prove the samething, because, both the composts, i.e. phosphated municipal rubbish and leaf compost, have been prepared through the incorporation of phosphate, have given higher yield in comparison to unphosphated municipal rubbish. The difference between the yield of these two phosphated composts, i.e. phosphated municipal rubbish and leaf compost, may be due to the presence of higher amount of phosphate in the phosphated municipal rubbish.

It has also been observed that more beneficial results have been obtained when the composts are add-d at the rate of 10 tons/acre than at 5 tons/acre. In the case of 5 tons/acre also the effectiveness of the different composts on the yield of barley grains is the same as in the case of 10 tons/acre.

Dhar and coworkers have obtained a marked fixation of nitrogen and humus formation in experiments where molasses (C/N ratio 40 or more), cowdung (C/N ratio 20), wheat straw (C/N ratio 65) were directly added to the soil. Since with these materials added to the soil, not only the humus corresponding to the originally present nitrogen but also an additional amount corresponding to the fixed nitrogen, is added, it is clear that with these materials, the total nitrogen and humus added to the soil always exceed the nitrogen and humus added in the manure. Moreover, as the carbonaceous compounds act as marked protein sparsers in the soil, the process of ammonification, nitrification etc. of the protein matter, are slowed down and losses of nitrogen will be reduced to the minimum. Therefore, in these cases subsequent crops will be benefitted even without addition of any manure as is observed in the classical Rothamsted experiment, and elsewhere.

From these pot experiments we have come to the conclusion that incorporation of phosphated compost rather than the unphosphated compost to the soil is superior for the yield of barley grains and straw. But due to the addition of decomposed organic matter to the soil, the humus capital is not increased much.

REFERENCES

1. Swenson, R. M., Cole, C. V. & Sieling, D. H., *Soil Science*, 67, 3 (1949).
2. Struthers, M. M. & Sieling, D. H., *Soil Science*, 68, 212 (1950).
3. Aslander, A., *Trans. Internat. 4th Congr., Soil Science*, 2, 153.
4. Das, S., *Ind. J. Agri. Sci.*, 15, 42 (1945).